Final Report

On

Development of Species Profiles for Selected Organic Emission Sources

Volume I: Oil Field Fugitive Emissions

Prepared by

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Contract no. A832-059

Development of Species Profiles for Selected Organic Emission Sources

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California Polytechnic State University

Prepared for California Air Resources Board

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ABSTRACT

This project involved the characterization of fugitive emissions from three source categories. Category 1 sources comprised emissions from California oil production facilities. Site selection criteria were developed, and resulted in the generation of a prioritized list of locations where emissions from light, medium and heavy crude petroleum operations would be sampled. At each site, samples from wellhead, pipeline, processing and storage systems were obtained. Specific components for sampling were pre-screened for positive hydrocarbon emissions using a portable hydrocarbon analyzer. The sampling methodology involved collection of 38 samples in evacuated stainless steel canisters. Detailed emission species profiles were determined by gas chromatography, with flame ionization detection. Peak identification was based on retention times, as well as separate gas chromatographic runs using a mass selective detector.

Category 2 and 3 sources included exhaust from utility and heavy-duty engines. The selection of 20 samples, based on estimates of engine populations in California, was described. The design and fabrication of a portable exhaust dilution system was discussed. Diluted exhaust from selected engines was sampled simultaneously for hydrocarbons and aldehydes. Diesel engines were additionally sampled for higher hydrocarbons. Hydrocarbon species were collected into evacuated stainless steel canisters. Aldehydes were absorbed into midget impingers containing DNPH/acetonitrile. High molecular weight hydrocarbons from Diesel exhaust were adsorbed in sorbent tubes filled with XAD-2 resin. Hydrocarbons were speciated by gas chromatographic techniques, as with Category 1 sources. Analysis of DNPH-aldehyde derivatives was performed using high performance liquid chromatography. Extracts from the XAD-2 resin were analyzed by gas chromatography, using a mass selective detector.

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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SUMMARY

In accordance with the Request for Proposal issued by the California Air Resources Board, this project involved the characterization of hydrocarbon and aldehyde emissions from a variety of sources. This report deals with Task 1 of that project, the development of a plan for sampling and analysis, as well as the Task 2 implementation of the approved sampling plan. Sources to be sampled were divided into three categories:

Category 1 - Oil Production Fugitive Emissions

Category 2 - Utility Engine Exhaust

Category 3 - Farm and Heavy-Duty Engine Exhaust

CATEGORY 1 SOURCES

As originally proposed, 38 samples from this category were to be collected and analyzed. The numerous components in an oil production field were segregated into "systems". These systems were classified as wellhead, pipeline, processing and storage. Each of these systems is progressively farther from the well than the preceding system. A sampling matrix was developed, consisting of various systems in fields producing light, medium and heavy crude oil. Samples from two secondary sumps were collected from a flux chamber in SUMMA electropolished, evacuated stainless steel canisters. Storage tank headspace samples were collected in evacuated steel canisters. Samples from other systems were obtained by isolating the selected component(s) with a Teflon shroud, and collecting the shroud effluent in evacuated steel canisters. Additional samples from several sources were taken by direct connection of the evacuated canisters to pipe fittings in the distribution lines, using Teflon tubing. Analysis for desired hydrocarbon constituents were performed using a variety of validated chromatographic methods.

CATEGORY 2 AND 3 SOURCES

Using estimates of engine populations in California, a ranking of these sources was developed. Classification was based on engine type, rather than equipment type. A total of 12 samples from Category 2, and 8 samples from Category 3 was recommended for sampling. Sampling for these sources involved dilution of the engine exhaust in a portable mini-tunnel. Hydrocarbons were collected in evacuated stainless steel canisters, while aldehydes were derivatized in DNPH/acetonitrile fileed midget impingers.. High molecular weight hydrocarbons were adsorbed in XAD-2 sorbent tubes. Hydrocarbon analysis were performed using gas chromatographic methods. Aldehyde derivatives were analyzed using high performance liquid chromatography. Extracts from XAD resin were analyzed by GC-MS. Details on this portion of the study are reported separately, in Volume II of this report.

Final Report, Task 1

I. Introduction

The general objective of this project was "to develop improved hydrocarbon species profiles for oil production equipment, and exhaust from utility and heavy-duty equipment". (ARB RFP, Feb. 1988). These species profiles, when multiplied by the appropriate emission rate factors, will yield detailed information on the mass emission rates for specific compounds. This report is divided into two volumes. The first volume deals with Category 1 sources (Oil Field Fugitive Emissions). The second volume discusses all aspects of Category 2 and 3 sources (Engine Tests). To address the various technical aspects of the project, a team of researchers was assembled. Team personnel, and their primary responsibilities, are shown in Figure 1.

II. Category 1 Sources

A. Site Selection Criteria

Efforts in this category were aimed at extracting hydrocarbon profiles from a variety of fugitive emission sources associated with petroleum production operations (Figure 2). There are several classification methods by which California oil production facilities may be grouped. The first of these methods involves classification by type of oil produced. Table 1 illustrates how the American Petroleum Institute (API) gravity may be used to divide crude oil production into light, medium and heavy categories. API gravity is inversely related to the specific gravity of the oil, as shown in Figure 3. Examination of the distribution of oil fields in California (Figure 4) reveals another potential classification scheme. There are three regions in which oil fields appear to cluster: the Salinas Valley (Coastal), the San Joaquin Valley, and the Los Angeles Basin. Figure 5 contains information on the size of the major oil fields in California. It was certainly desirable to have the major fields be included in this study. Thus, the Ventura, Elk Hills and Wilmington fields were targeted for further investigation. While there may be variations in API gravity within a given field, an estimate of the average composition of various fields was developed (Table 2). Moving to a list of major oil producers in California (Table 3), contacts were initiated with personnel from Shell, Chevron, Bechtel, Texaco, Union Oil, and THUMS Long Beach Company. Details of key personnel contacted will be found in Appendix A. Discussions with these people helped clarify the nature and API gravity produced in a large number of lease fields. Combining the information on crude oil type with location produced a sampling matrix, shown in Table 4. The ARB-approved work plan allowed for sampling and analysis of 38 Category 1 Sources. The use of budgeted funds to collect all samples in duplicate did not appear to be an efficient method of quality assurance. Instead, we collected replicates from a single component in a test field. Results from the analyses of these samples provided an estimate of uncertainty in the entire sampling/analysis chain.

Figure 1 - Personnel

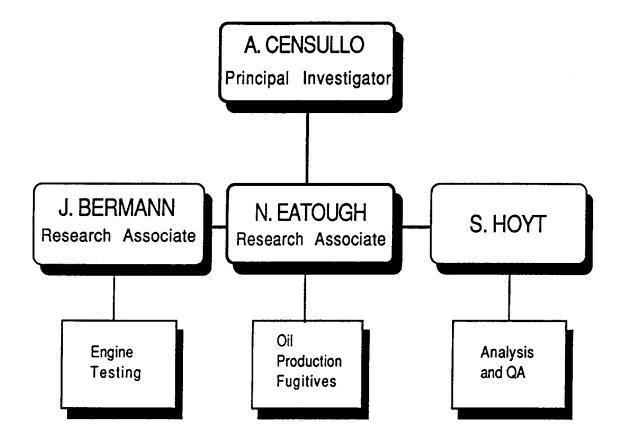


Figure 2 - Category 1 Sources

- Tanks
- Pipeline valves / fittings from light medium heavy
 Sumps and pits

Table 1 - API GRAVITY OF SELECTED FIELDS

0.85 ' fremebottom	BASIN	\mathtt{API}^0
Cat Canyon	Coastal	4
Midway-Sunset (shallow)	San Joaquin	12
San Ardo	Coastal	12
Kern River	San Joaquin	13
McKittrick Main Area	San Joaquin	15
Santa Maria Valley	Coastal	16
Torrance	LA	16
Wilmington (shallow)	LA	18
Whitter	LA	18
Richfield	LA	22
Coyote East	LA	22
Montebello	LA	22
Huntington Beach	LA	24
Belridge South	San Joaquin	25
Elk Hills	San Joaquin	· 25
Inglewood	LA	26
Midway-Sunset (deep)	San Joaquin	26
Long Beach	LA	27
Coyote West	LA	28
Coalinga Nose	San Joaquin	32
Dominguez Hills	LA	32
Rosecrans	LA	32
Wilmington (deep)	LA	32
Santa Fe Springs	LA	33
Montebello (deep)	LA	36
Kettleman Hills	San Joaquin	38
Coles Levee	San Joaquin	40
Rio Bravo	San Joaquin	40
Paloma	San Joaquin	50

Figure 3 - API Gravity

OAPI =
$$\frac{141.5}{\text{specific}} - 131.5$$
gravity

OAPI	specific gravity	Example
10	1.000	water
20	0.934	heavy crude
30	0.876	light crude

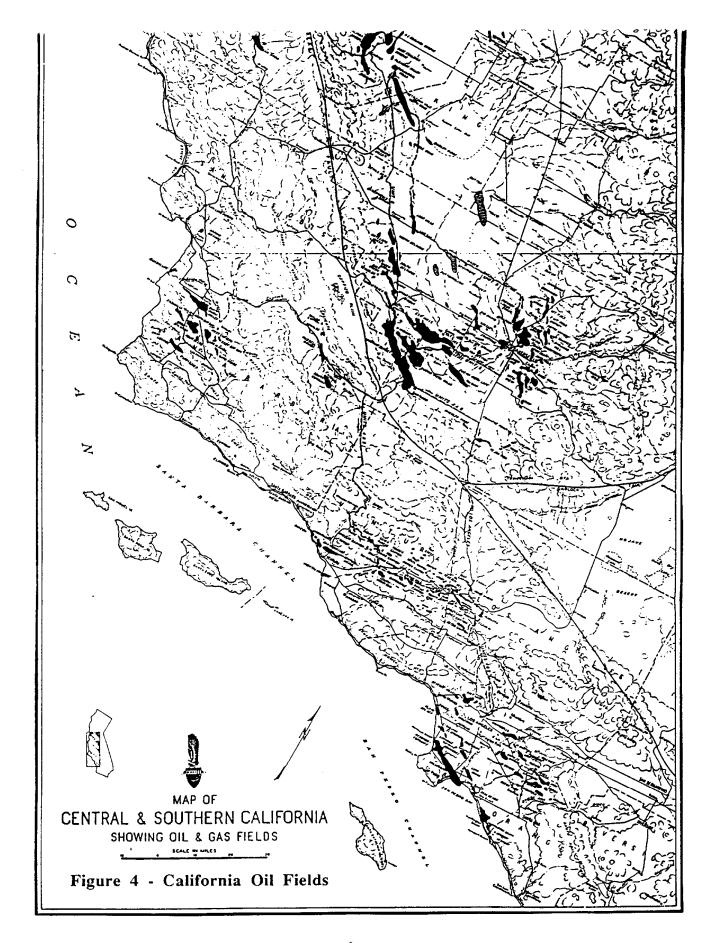


Figure 5 - Size of Major Oil Fields

CALIFORNIA'S GIANT OIL FIELDS (Fields with ultimate recovery of 100 million barrels or more)

	Kern River River Hills	(Coyote West
	Caryon Ventura	Wilmington
2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	* ******* ****** ****** ****** ****** ****	ed

	11610	DISCOVERED	(Mbb1)	(Pbb) (12/31/87)	(Mbb1)	(1981)
1	Mileington Hidaay Susset Kern River Bullangton Beach Long Beach	1932 1894 1899 1920	2, 261, 472 1, 871, 712 1, 158, 042 1, 060, 167 907, 115	526, 686 430, 645 77, 874 77, 874	32,109 57,109 57,109 65,050 6,050 2,580 1,050 6,	2, 055 9, 075 7, 220 9, 94 115
	Vontura Els Ells Coalinga Bucha Vista Belidge, South	1919 1811 1890 1909	887, 658 854, 145 743, 996 645, 722 616, 000	103,367 1 162,399 1 182,939 1 184,948	7, 279 40, 572 10, 384 1, 515 63, 562	570 1, 217 2, 343 1, 035 6, 161
	Santa fe Springs Coalings, Last, Extension Kettleman North Dore San Ardo Brea-Olinda	1919 1938 1928 1947 1860	612, 295 497, 452 463, 485 403, 692	9,959 18,655 1,150 126,053	1,030 1,030 1,030 1,043 2,320	16.52 2.62 2.63 2.63 2.63 2.63 2.63 2.63 2.6
	Inglewood Cai Canyon Cos inguez McKitzi Ck Young Poso	1924 1924 1923 1939 1926	343,006 285,509 268,794 264,032 256,633	57, 042 49, 490 8, 052 93, 485 85, 869	3,078 2,940 2,860 7,094	356 612 11,067 500 500
	Coyote, West Cuyama, South Orfance Dos Cuadras Offshore Seal Beach	1909 1 1949 1 1922 1 1924	249, 205 217, 567 210, 358 203, 204 202, 204	6,317 37,204 63,352 14,994	830 519 1,681 5,064 946	1266
27.	Santa María Valley Cyrtic Maxchelln Riccheld Dost Eills	19934	196,302 191,494 191,197 186,369 172,551	42,148 38,454 10,807 28,971 67,292	1, 902 6, 908 1, 612 5, 293	1,145
25.52	Kern Front Ordit Colse Levee, North Rincon South Mountain	1912 1912 1918 1918 1927	171, 574 164, 968 159, 800 147, 625	57, 369 11, 154 17, 110	1, 100 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	3555
53.55	Edison Beverly Bills Alo Bravo Fruitvale Greeley	1928 1900 1937 1938 1936	132,961 119,710 115,899 114,937	28, 117 44, 420 1, 474 1 14, 283 2,001	2,529 2,213 183 183 2,560 183 2,56	121 121 121 121 121 121
#4444	Coyote, East Elwood Round Mountain Sm. Hignelito Carpinteria Offshere (total)	1928 1927 1927 1931	108,076 105,276 96,010 95,208 85,411	13, 753 5, 604 5, 756 146, 630 31, 979	625 1 365 1 261 1 945 1 2,686	26.7 26.7 11.9
20.00	Belildge, North Eondo Offshore Poso Creek Toulusne Beta Offshore	1912	82,485 79,376 79,005 172,721 103,704	45, 458 122, 522 25, 091 33, 750 180, 568	2,430 9,587 836 7,946	2 2 2 2 2 2

1.1

THIRTY LARGEST OIL PRODUCERS IN CALIFORNIA - 1987*

	PRODUCER	OIL PRODUCTION (Mbb1)
i 3.	Texaco, Inc. (2) Bechtel Petroleum Operations Inc. (4)a/ Chevron U.S.A. Inc. (3)	85,902 48,492 40,654 40,057 22,127
9.		20,953 16,320 16,177 15,835 10,732
12. 13. 14.	ARCO Oil and Gas Company (11) Celeron Oil and Gas Company (15) Union Pacific Resources Company (14) b/ Exxon Corporation (16) Berry Petroleum Company (NA) c/	6,980 4,716 2,994 2,731 2,517
17. 18. 19.	Conoco, Inc. (17) M. H. Whittier Corporation (18) Long Beach Oil Development Company (19) McFarland Energy Inc. (22) Cities Service Oil Company (21)	2,275 2,259 1,844 1,023 881
22.	Tannehill Oil Company (NA) Mission Resources (20) Occidental Petroleum Corporation (25) Powerine Oil Company (Operator for the City of Long Beach) (24) West Newport Oil Company (26)	805 726 672 670 661
28.	Petro-Lewis Corporation (13) Signal Hill Petroleum (30) Chase Production Company (NA)	638 506 440 416 403

Does not include federal OCS figures. Also, total production from unitized operations is credited to the unit operators and not allocated to the other unit participants; therefore, production figures are overstated for unit operators and understated for other unit participants.

⁺ Numbers in parentheses indicate last years rankings.

a/ Production shown for Bechtel Petroleum Operations Inc. includes Chevron U.S.A. Inc's portion of Elk Eills production, which was 8,841 Mbbl., and is not included in Chevron's total.

b/ Formerly listed as Champlin Petroleum Company.

c/ Includes figures formerly reported separately under Berry & Ewing, Berry Holding Co., Berry Ventures, Big Ten Oil Co., Ethel D.Co., and Berry Oil Co.

Table 3 - Sampling Matrix for Oil Production Facilities

Site	# of samples	Operator	Basin	Oil type	Preferred, alternate
1. Santa Maria	4	Union Oil	Coastal	Heavy	preferred
2. Ventura	4	Chevron	Coastal	Heavy	preferred
3. San Ardo	4	Texaco	Coastal	Heavy, sour	alternate
4. Coyote West	6	Chevron	LA	Medium	preferred
5. Wilmington	6	THUMS	LA	Heavy	preferred
6. Elk Hills	8	Bechtel (DOE)	San Joaquin	Light	preferred
7. Bellridge	8	Shell	San Joaquin	Light	preferred
8. Kern River	8	Texaco	San Joaquin	Medium	alternate

B. Component Selection Criteria

Once suitable sites had been identified, selection of the mix of components to sample became the next consideration. Using previous related studies (Figure 6) as a starting point, an inventory of possible components was generated (Figure 17). The distribution of various components is shown in Figure 8. Reported incidence of leaks for these components is shown in Table 5. A Rockwell study categorized components into 9 types, and 51 styles (Figure 9). It became apparent that the 38 budgeted samples could not be selected on a component basis. An alternative approach is to consider the numerous components arranged into systems of varying complexity and function. Within each system, the nature of fugitive emissions from various components will be identical (or at least very similar). For example, the composition of fugitive emissions from a leaking gate valve at the wellhead will be the same as the emissions leaking from a flange a few inches away. Consider the same valve/flange combination at a storage tank. The emissions will now reflect the composition of the tank's contents. Systems to be sampled include wellhead, pipeline, processing and storage. Discussions with ARB at the 2/9/89 meeting confirmed that this approach should yield data compatible with the project's goal. At each site identified in the previous section, components from each system would be sampled, up to the amount of samples allotted per site. This process allowed for more efficient use of the limited number of samples budgeted for analysis than would be possible in a component-driven sample selection process. Table 6 represents a summary of all oil field samples collected.

C. Sampling Methodology

The general steps involved in sampling fugitive emissions are outlined in Figure 10. Facility maps, and piping and instrumentation drawings will provide an estimate of where the maximum density of components to be sampled are located. Previous studies have indicated that usually these drawings are either not available or not current enough to be useful. Consequently, we performed final component selection on-site, using a rapid screening method to identify potential components. Oil field personnel at each site provided assistance in locating sampling sites meeting our selection criteria. Each selected component was tested using a Gastech Analyzer to verify the presence of hydrocarbons. The component would then be sampled, subject to conforming to the desired systems and sample numbers at the site. Sample characteristics, including temperature, size, estimated leak rate (from soap leak test), and condition were recorded. At least 3 photographs were taken of each component sampled. These showed the component in isolation, its location in a system, and the sampling device used. Appendix B shows some selected sampling setups.

1. Sampling Fittings

While there is no "standard" method for sampling components of varying sizes and shapes for fugitive emissions, past studies have isolated the desired component, using a "shroud" of inert sheeting. An example of such a sampling system is shown in Figure 11. If the component has a leak rate in excess of 1 liter/minute, the emission will purge and inflate the shroud in a reasonably short period of time. This "direct" approach will not work for small leaks. An "indirect" method for sampling small leaks involves capturing the emission with a stream of dilution air. Previous studies have used ambient air for dilution. This required an independent analysis of ambient air for each component sampled. The proposed sampling system to be used in this study is illustrated in Figure 12. The component shrouds were fabricated from Teflon (FEP) bags. A quantity of 12" x 12" and 24" x 36" bags were prepared, as illustrated in Figure 13. A cylinder of ultra-zero air (<0.1 ppm hydrocarbons) was used for the source of dilution. A size 3 cylinder holding 30 cubic feet at 2000 PSI, and weighing less than 30 pounds was

Figure 6 - Previous Oil Production Fugitive Emission Studies

- 1. RADIAN CORP (EPA), 1978
- 2. EMSI (ROCKWELL), 1979
- 3. KVB (ARB) , 1980
- 4. ERT (WOGA) , 1983
- 5. EMSI (MIN. MGMT. CORP), 1988

Figure 7 - Oil Production Components

Oil Production Equipment

I. Tanks

A. Storage

Fixed roof

Floating roof
Internal floating cover

Variable space

B. SurgeC. Flotation

D. Vapor recovery

E. Wash

II. Pipeline Valves and Flanges

A. Valves

Gate Ball Plug Globe Needle Check Butterfly Relief

B. Flanges

Raised face Flat face API ring Access

III. Sumps and Pits

- A. Cleanout sumpsB. Produced water sumps
- C. Sucker rod pitsD. Well cellars



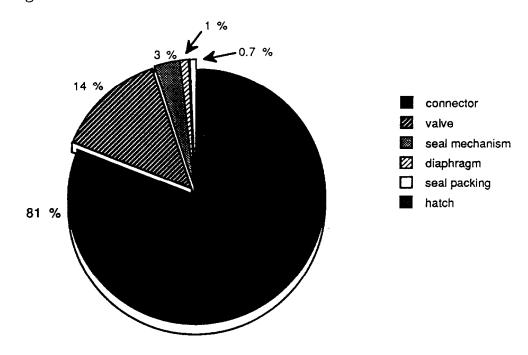


Table 4 - INCIDENCE OF LEAKS

(From 1979 EMSI Study)

	Number of Components Tested	Percent Leaking
Valves	9427	6.4
Flanges	54,694	2.8
Tank Hatches	170	2.4
Seals	474	30.6
Pits	26	100

Figure 9 - Detailed Component Categories

		Component Types	<u>Systems</u>
1 2 3 4 5 6 7 8 9	VL CN SG MT HA SP DI SM PP	Valve Connection Sight Glass Meter Hatch Seal Packing Diaphragm Sealing Mechanism Sump, Pile, Pit, Etc.	1 Well head2 Pipelines3 Processing4 Storage
7	rr	Jump, File, File, Elle,	

Component Styles

1- 1	٧L	GATE	Gate	5- 1 5- 2	HA HA	FLFF FLGA	Flanged Flat, Soft Gasket
1- 2	٧L	MULT	Multi-Directional				
1- 3	٧L	BALL	Ball	5- 3	· HA	THIF	Thief
1- 4	٧L	PLUG	Plug			200	O otenia dia Bed
1- 5	٧L	GLBE	Globe	6- 1	SP	RERO	Reciprocating Rod
1- 6	٧L	NDLE	Needle	6- 2	SP	ROSH	Rotating Shaft
1- 7	٧L	CHCK	Check	6- 3	SP	MESL	Mechanical Seal
1-8	٧L	BTFY	Butterfly	6- 4	SP	WLHD	Wellhead, Stuffing Box
ī- 9	٧L	RELF	Relief				
1-10	٧L	CHOK	Choke	7- 1	DI	VLOP	Valve Operator
1-11	٧L	BEAN	Bean Choke	7- 2	DI	OPRS	Differential Pressure
1-11	76	OLAN					Sensing
2- 1	CN	FLFF	Raised or Flat				
			Face Flange	8- 1	SM	GATE	Gate
2- 2	CN	FLRI	Ring Flange	8- 2	SM	MULT	Multi-Directional
2- 3	CN	FLBO	Flanged Bonnet	8- 3 8- 4	SM	BALL	Ba11
2- 4	CN	THRO	Threaded	8- 4	SM	PLUG	Plug
2- 5	CN	GRVD	Grooved	8- 5	SM	GLBE	Globe
2- 6	CN	FRIC	Friction	8- 5 8- 6	SM	NDLE	Needle
2- 7	CN	GASK	Gasket	8- 7	SM	CHCK	Check
2- 8	CN	UNIN	Union	8-8	SM	BTFY	Butterfly
2- 9	CN	LAND	Landing Flange	8- 9	SM	RELF	Relief
2-10	CN	TUBE	Tubing	8-10	SM	CHOK	Choke
			O-Ring	8-11	SM	BEAN	Bean
2-11	CN	ORIN		0 11	J		
2-12	CN	FLGA	Flat, Soft Gasket	9- 1	РР	OPSU	Open Sump
2 1	SG	GLSS	Glass Type	, ,	• •	J. 70	(Produced Water)
3- 1	20	GESS	arezz ilbe	9- 2	ρр	CLSU	Closed Sump
	ur	בו טוו	C1 au	9- 3	PP	WLCL	Well Cellar
4- 1	MT	FLOW	Flow	9- 4	pp	COSU	Clean-out Sump
4- 2	MT	TURB	Turbine Type Flow	9- 4 9- 5	PP	OPTK	Open Roofed Tank
				3- 3	rr	UPIN	ohen voored rank

Table 5- Oil Field Sampling Sites

sample #	APIO	location	method	comments
Kern River	 			
OF-1	13.5	gage tank	headspace	roof hatch
		(AWT143)	<u> </u>	
OF-2	13.5	well 406	bag valve	
OF-3	13.5	well 406	bag valve	duplicate of OF 2
OF-4	13.5	shipping tank #40	headspace	roof hatch
OF-5	13.5	surge tank	headspace	roof hatch
OF-6	13.5	well 271	bag valve	well duplicate
Elk Hills				
OF-10	23	tank 11105	bag sampling port	headspace
OF-11	23	compressor	canister direct	vapor recovery: NPT connection
OF 12	- 22	FR1364		NP1 connection
OF-12 OF-13	23 36	separator 11044 tank 11470	same as OF-10	Stevens zone
OF-13 OF-14	36	separator 14255	Same as OF-10	Stevens zone
OF-14 OF-15	36	tank 14217	bag sampling port	headspace
OF-15	22	tank 53579	bag 2" port	steamflood operation
OF-16 OF-17	22	test separator	bag meter valve	steamflood
Or-17	22	test separator	bag meter varve	produced gas
Belridge	 			produced gas
OF-20	33	tank LOTS 201	canister direct	20 well composite
0. 20		tmm 2010 201		vapor
OF-21	33	well 548G-34	bag valve	casing gas
OF-22	26	tank LOTS 209	canister direct	1/4 NPT gauge port
OF-23	21	well 551-A33	gas valve	casing gas
OF-24	28	tank LOHF	canister direct	20 LOTS composite
OF-25	13	tank DEHY #27	canister direct	heavy field composite
OF-26	13	tank HOTS 113	bag valve port	50 well heavy
				composite
OF-27	13	tank HOTS 192	bag valve port	50 well heavy
				composite
Cat Canyon		11.50		
OF-40	14	well 53	bag valve	casing gas
OF-41	14	well 53	bag valve	tubing gas
OF-42	14	vapor recovery	bag valve flux chamber	composite of all tanks
OF-43	14	sump, inlet end		
OF-44 Ventura	14	sump, outlet end	flux chamber	
OF-50	29	tank	bag valve	100 well composite
OF-50	29	well L-131	bag valve	casing gas
OF-51	29	vapor recovery	canister direct	field composite
OF-53	29	vapor recovery	canister direct	shipping tank
Wilmington		- apol recovery	Junior anoct	July min
OF-60	18	Pier J sump	flux chamber	
OF-61	18	tank TK 003	headspace	roof hatch
OF-62	18	FWKO tank #3	canister direct	
OF-63	18	well J-341	bag valve	casing gas
West Coyote				3.8
OF-70	28	AWT tank 105	bag valve	
OF-71	28	work tank #1	headspace	roof vent
OF-72	28	stock tank	bag port	manometer port
OF-73	28	vapor recovery	bag valve	field vapor recovery

Figure 10 - FUGITIVE EMISSIONS SAMPLING PLAN

- STUDY FACILITY MAPS / DRAWINGS
- INVENTORY AND "SOAP TEST" COMPONENTS
- CHECK LEAKERS WITH OVA
- SAMPLE LEAKERS PER COMPONENT MIX
- DOCUMENT SAMPLED COMPONENTS

Figure 11 - Literature Sampling System

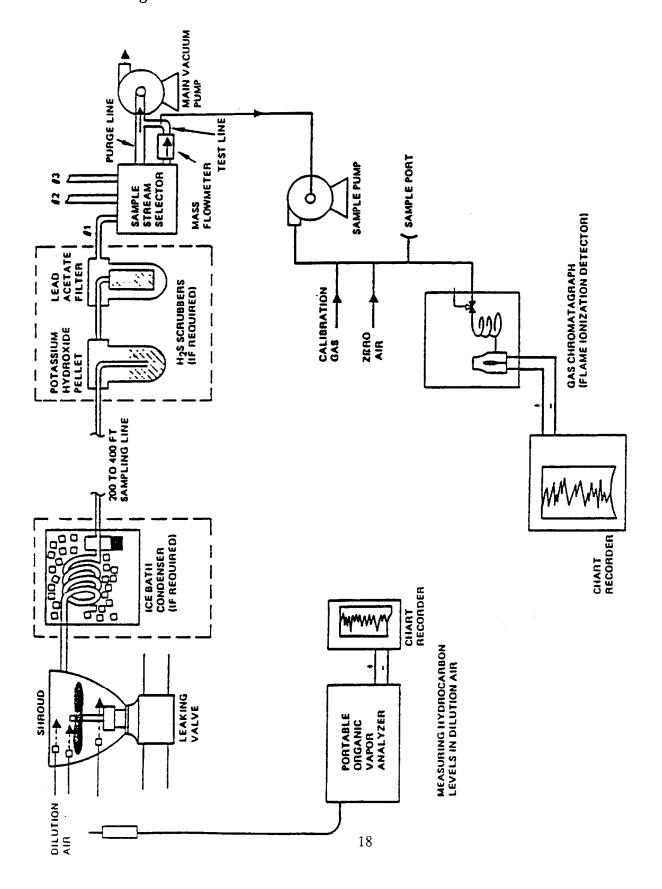


Figure 12 - SCHEMATIC REPRESENTATION OF SAMPLING FOR VALVES AND FLANGES

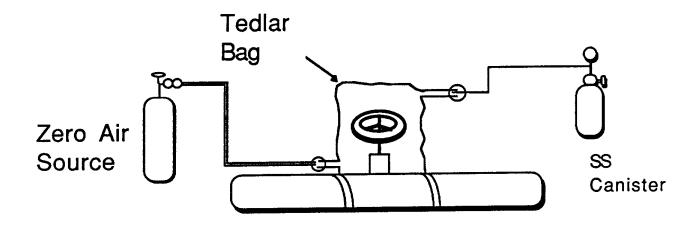
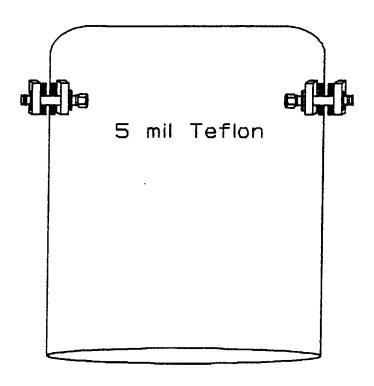
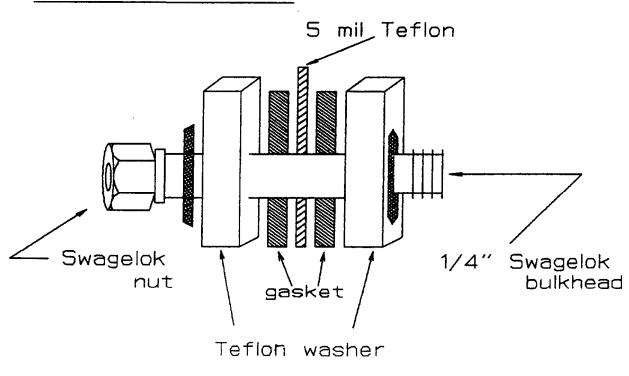


Figure 13 - Teflon Bag Construction

TEFLON SAMPLING BAG



FITTING DETAIL



20

brought to each oil field site. A manual control valve attached to the cylinder ensured contamination-free and reliable delivery of the zero air. In using this scheme, resources need not be spent on determining ambient concentrations in dilution air. Once the shroud has been filled with emissions, sampling from the shroud into an evacuated, SUMMA electropolished stainless steel canister (Figure 14) may be started. The long-term stability of hydrocarbons in these containers has been well-established1. Since no sampling pumps are needed in the field, contamination or degradation of the collected samples is virtually impossible. Pre- and postsampling canister pressure checks were performed in the field, using a portable vacuum/pressure gauge. These pressures were verified at the analytical laboratory. In practice, purging of sampled components (indirect emission sampling) proved to be unnecessary, due to the large "leak rates" of components selected for sampling. Consistent with the objectives of the program, representative vapor samples were obtained at selected points in the overall process. While the exact method of sampling fugitive emissions depended on the source, several general methods were employed. In some instances, existing pipe fittings were connected to the evacuated stainless steel canisters by 0.25 inch diameter Teflon tubing equipped with stainless steel Swagelok fittings. Sampling flowrate could be controlled by the needle valve on the canister. For cases in which no suitable pipe fittings were available, pipe ends equipped with shutoff valves were often located. In these cases, the exposed pipe end was surrounded with a Teflon bag, secured with a large rubber band. The sampling bag was then purged and inflated with source emissions. This "buffer" volume was sampled into an evacuated canister connected to the bag by a length of 0.25 inch Teflon tubing. These approaches worked well for sources which were above atmospheric pressure. Samples ranging in pressure from 50 PSI to a few inches of water were successfully sampled by these methods. Sampling was normally continued until canister pressure, monitored by an attached pressure/vacuum gauge, reached atmospheric pressure.

2. <u>Sampling for Sumps and Pits</u>

In order to obtain samples of fugitive emissions from sumps and pits, some sort of emission isolation (flux) chamber is required. The U.S. EPA² and California ARB³ have validated designs used for emission rate measurements. For the sump samples, an ARB sump sampler used in previous studies was modified. The existing acrylic flux box was removed. A new flux chamber, fabricated from a 14" diameter stainless steel hemisphere, was prepared, as shown in Figure 15. A latching valve was incorporated into the design to allow sampling to be initiated remotely. The sampling canister was located on the sump sampler to minimize the potential for contamination or losses in the sampling line. A circuit to produce pulses of the proper characteristics to operate the latching valve was constructed (See Figure 16). The circuit was powered by two 9 volt transistor batteries. These batteries provided several hundred activation cycles during testing without appreciable loss of working voltage. Pulses were approximately 50 milliseconds in duration. An umbilical was necessary to convey air and latching voltage pulses to the sampler. Three 1/4" Teflon lines, and one four conductor shielded cable were bundled together with nylon cable ties. One Teflon line was used with a zero air source to control the pneumatic pistons which ultimately raised and lowered the attached flux chamber. A second Teflon line provided the ultra-zero sweep air to the flux chamber. The third Teflon line returned the flux chamber purge gas to shore for testing. The total length of the umbilical was 50 feet. The aluminum pontoons of the ARB sampler were moved apart several inches to allow for the mounting of the new flux chamber. The assembled device was tested for buoyancy on an irrigation pond at Cal Poly. The final configuration proved to be stable and buoyant.

Figure 14 - Stainless Steel Canister Design

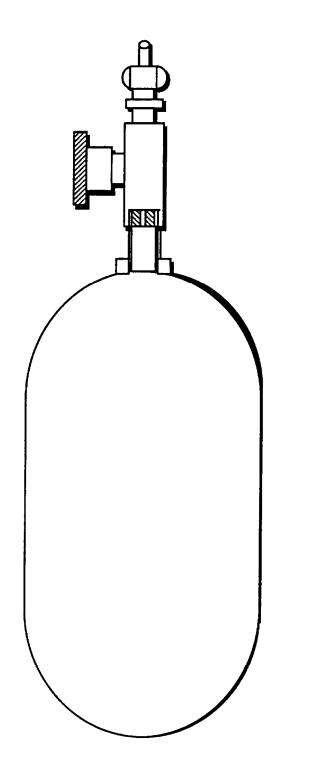


Figure 15- Flux Chamber Design

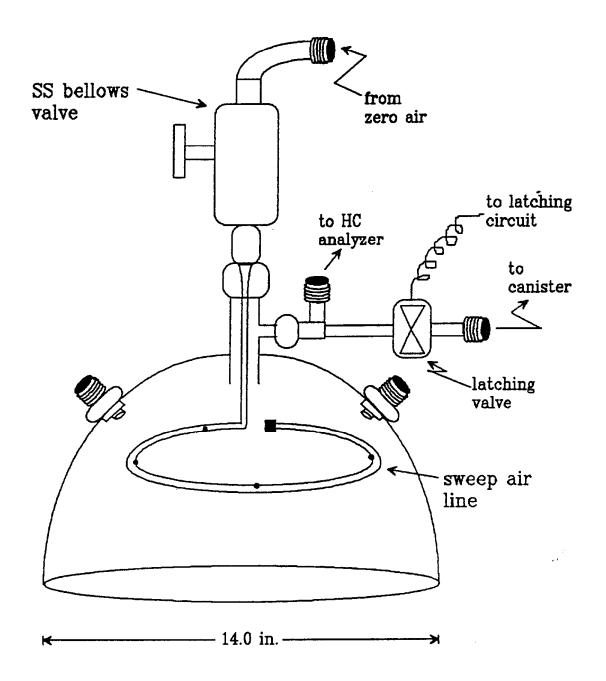
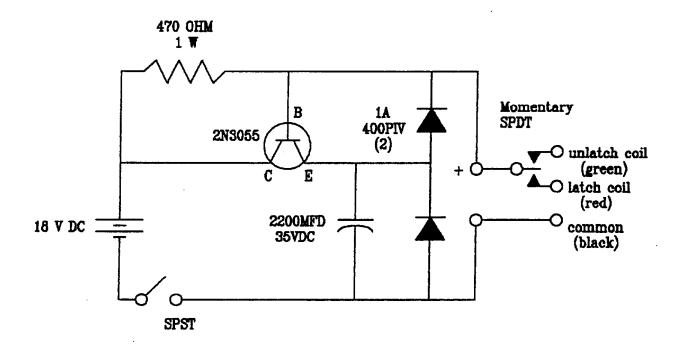
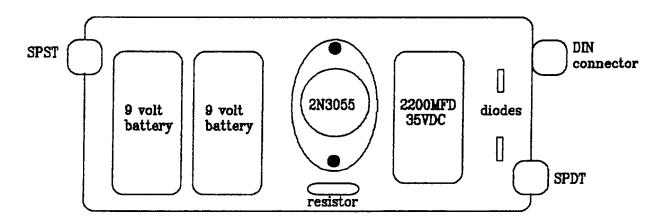


Figure 16 VALVE LATCHING CIRCUIT

schematic



component placement



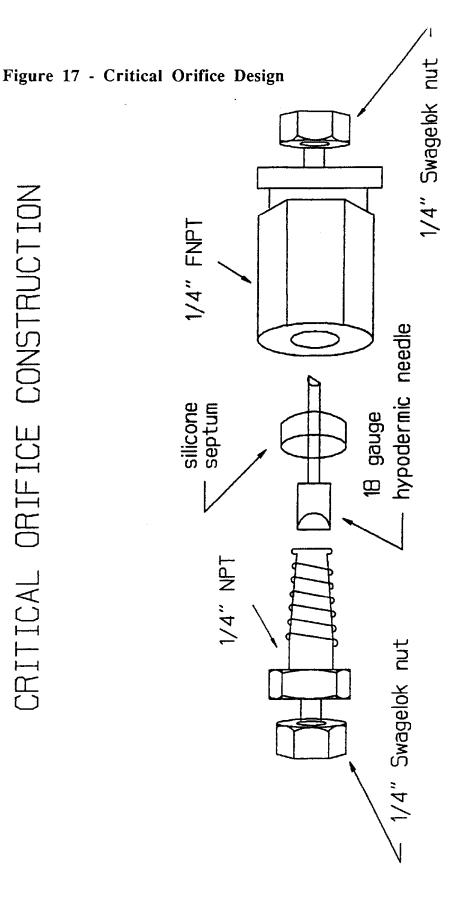
Sampling was conducted at a flow rate of 5 liters/minute, following the suggested EPA protocol. Chamber volume was roughly 15 liters, so the residence time at this flowrate was on the order of 3 minutes. According to the adopted protocol, sampling would begin after 4 chamber volumes had been purged (12 minutes). At the end of 12 minutes, a sample was pulled into an evacuated stainless steel canister, via the latching valve. In order to prevent the canister from drawing air at a greater rate than was provided (5 liter/minute), some method of flow control was required. Although the sampling canisters used were fitted with bellows valves, it proved impossible to reliably control flow by partially opening the valves. A limiting orifice was fabricated from an 18 gauge hypodermic needle. See Figure 17 for construction details. The canister metal bellows valve was kept in the fully open position at all times. The latching valve enabled/disabled flow, while the limiting orifice controlled the flow rate into the canister. This simple approach worked reliably in field tests. The canister thus equipped would fill in roughly 90 seconds, for an average flow rate of 3.2 liters/1.5 min = 2.1 liters/min.

Prior to use in the field, a test to explore possible pressure buildup inside the chamber at the anticipated flowrate was undertaken. The flux chamber was suspended in a basin of water, so that the lower lip was immersed about one inch below the liquid surface. Pressure inside the chamber was measured with a Magnehelic gauge while 5 liters/minute of sweep air was admitted to the chamber. The Magnehelic gauge indicated a differential pressure of less than 0.2 inches of water, which was deemed satisfactory. This sampling system utilized the same zero air source and stainless steel canisters as used for sampling fittings (vide supra). Samples presented to the laboratory for analysis thus had identical sample handling procedures, regardless of whether the samples were taken from shrouds, sumps/pits or storage tanks (vide infra). Since secondary sumps comprise approximately 99% of total sump areas, and since most secondary sumps have areas in excess of 1000 square feet, secondary sumps larger than 1000 square feet were used to satisfy sampling requirements for sumps. Previous work³ involving the characterization of hydrocarbon emissions from sumps failed to show a clear dependence of emission rate or composition on location within a sump. Consequently, we proposed testing each sump at a single location. If accessibility permitted, a spot near the center of the sump was selected. The composition at the center of the sump is more likely to be representative of the average sump area than locations near a sump inlet or outlet. At each location, a sketch and photograph(s) were produced. Pertinent information about the sump, including temperature, oil depth, and size will be recorded on a data sheet prior to sampling. Detailed protocols for sampling these components will be found in Appendix C. The use of sumps in California petroleum fields has been declining dramatically in recent years. Consequently, only two sumps were sampled in this study.

3. Sampling from Storage Tanks

Storage tanks have long been recognized as potentially large sources of fugitive emissions. Consequently, extensive work on storage tank design has produced alternatives which attempt to reduce the quantity of fugitive emissions. Some of these schemes such as the floating roof, produce systems in which accurate sampling for fugitive emissions is quite difficult. Since this project is more concerned with emission composition than emission rate measurements, a conceptually simple approach to collecting accurate samples from tanks was discussed with ARB. Regardless of tank design, if it leaks at all, it will leak the headspace of the tank. Thus, sampling the headspace inside the tank should provide all the information needed for this study. Conversations with personnel (Hagist and Rutledge, Appendix A) in petroleum operations confirmed that access hatches are located on top of storage tanks, and are readily accessible for

CRITICAL ORIFICE CONSTRUCTION



sampling headspace. At the 2/9/89 meeting, the Board approved of headspace sampling for storage tanks. Most of the tanks sampled in this study were equipped with access hatches on the roof. If the tank headspace were at atmospheric pressure, its contents were sampled into an evacuated canister by means of a short 0.25 inch diameter stainless steel probe inserted through the access hatch. In several cases, the tanks were maintained above atmospheric pressure by the vapor recovery system. Opening the roof hatch on tanks so equipped would require venting appreciable amounts of vapor to the atmosphere. In these cases, a sampling port external to the tank was located. The pipe end was bagged, and the emissions were sampled from this bag, as described earlier.

Detailed protocols for sampling fugitive emissions from oil production facilities may be found in Appendix C.

D. Quality Assurance

Quality assurance (QA) activities for Category 1 sources may be divided into three categories:

- 1. Pre-field sampling QA
- 2. Field sampling QA
- 3. Analytical QA

Pre-field activities included a complete checkout of all sampling system components. Data on the analysis of gas cylinders to be used were compiled. Data forms, sample labels and containers were located and prepared. To verify proper operation of the sump sampler, the flux chamber was placed on top of a clean sheet of Teflon, and zero air was allowed to flow through the system. This purge air was collected and analyzed, to verify the absence of background contamination. Prior to sample collection, all sample lines were thoroughly flushed with zero air. Adherence to the written protocols found in Appendix C enhanced the overall reliability and reproducibility of data obtained. Quality assurance activities pertaining to analyses are described in Appendix D.

E. Analytical Methodologies

A variety of analytical techniques were needed to quantitate the hydrocarbon species present in the oil field samples. This section summarizes the analytical methodologies used by the Project Subcontractor, Environmental Analytical Service, Inc. (EAS). Deatils and standard oerating procedures for the methods of analysis will be found in Appendix D.

Methane was analyzed using a molecular sieve 5A column, operated isothermally at 50 °C. Light hydrocarbons were separated using a ten foot column packed with phenylisocyanate on 80/100 mesh Durapack. Samples with high hydrocarbon content were analyzed on a 30 foot column containing 23 % SP-1700 on 80/100 mesh Chromosorb PAW. Heavy hydrocarbons were analyzed using a 100 meter fused silica capillary column.

Comparison of the light (packed column) and heavy hydrocarbon (capillary column) runs could be made using a number of peaks.in the C2 to C4 range. The heavy stationary phase loading of the 100 meter capillary column allowed for the separation of the lighter hydrocarbons. In this project, values for the light hydrocarbons (from C2 on) obtained from the capillary column run were used for all calculations shown in the Results section of the report. Values obtained from the analyses of light hydrocarbons on the two columns (packed and capillary) were generally comparable (within 10% of each other). In many instances, the capillary column allowed for the identification of peaks which were listed as "OTHER" by the packed column method. It became operationally simpler to utilize data from the capillary run to quantitate all hydrocarbon species (other than

methane), and this procedure obviously eliminated the effect of compounding and propagating analysis errors from two different analytical methods.

F. Oil Field Sampling

1. Kern River field

A site visit was planned to finalize sampling methodologies and location. The trip was conducted on May 12, 1989. Censullo and Eatough toured the facility with Tim Stoner of Texaco. Plans were made for sampling on July 10. The average API gravity of this field is 13.5°. Recovery method in this field is primarily steamflood. Six samples were taken, as outlined below.

Kern River				air temp	source temp
OF-1	gage tank (AWT143)	headspace	roof hatch	33º C	72º C
OF-2	well 406	bag valve		35° C	100° C
OF-3	well 406	bag valve	duplicate of OF 2	35° C	100° C
OF-4	shipping tank #40	headspace	roof hatch	35º C	69º C
OF-5	surge tank	headspace	roof hatch	35º C	36º C
OF-6	well 271	bag valve	well duplicate	36º C	100° C

2. Elk Hills field

Sampling at this site was conducted on July 17, 1989. Two producing zones were sampled. The SOZ zone has an API gravity of 22-25°; the deeper Stevens zone contains oil in the range of 30-35° API. The waterflood method is used for recovery in most of the field. A small scale steamflood project was also operating at that time. Seven samples were taken, as outlined below.

Elk Hills			•	air temp	source temp
OF-10	tank 11105	bag sampling port	headspace	29º C	29º C
OF-11	compressor FR1364	canister direct	vapor recovery: NPT connection	33° C	33º C
OF-12	separator 11044			30° C	30° C
OF-13	tank 11470	same as OF-10	Stevens zone	36º C	36º C
OF-14	separator 14255			36° C	44° C
OF-15	tank 14217	bag sampling port	headspace	35º C	35° C
OF-16	tank 53579	bag 2" sampling port	steamflood operation	33°C	33° C
OF-17	test separator	bag meter valve	steamflood produced gas	33º C	46º C

3. Belridge Field

Sampling was performed on July 24, 1989. Light, medium and heavy crude is produced in this field. Eight samples originating from light crude of 33° API gravity, a medium crude of 26-28° and a heavy crude of 13° gravity were taken. A portion of recovery is by waterflood, with the balance being primary production. Samples taken are described in the following table.

Belridge				air temp	source temp
OF-20	tank LOTS 201	canister direct	20 well composite vapor	34º C	34º C
OF-21	well 548G-34	bag valve	casing gas	33º C	39º C
OF-22	tank LOTS 209	canister direct	1/4 NPT gauge port	37°C	37º C
OF-23	well 551-A33	gas valve	casing gas	35° C	37° C
OF-24	tank LOHF	canister direct	20 LOTS composite	35º C	35° C
OF-25	tank DEHY #27	canister direct	heavy field composite	36º C	36º C
OF-26	tank HOTS 113	bag valve port	composite	37º C	110° C
OF-27	tank HOTS 192	bag valve port	50 well heavy composite	39º C	71° C

4. Cat Canyon Field

A pre-sampling visit was arranged for July 21, 1989. Sampling plans were discussed with Union Oil personnel, and facilities were toured. A sump was identified for testing. The sampling date was set for August 8. The field produces heavy crude, with an average API gravity of 14°. A total of 5 samples were obtained, as outlined below. Dr. Robert Grant (ARB) was present for this sampling episode.

Cat Canyon				air temp	source temp
OF-40	well 53	bag valve	casing gas	28º C	28º C
OF-41	well 53	bag valve	tubing gas	22º C	22° C
OF-42	vapor recovery	bag valve	composite of all tanks	27º C	27° C
OF-43	sump, inlet end	flux chamber		30º C	39º C
OF-44	sump, outlet end	flux chamber		32º C	43° C

5. Ventura Field

Texaco's Ventura Avenue Field was sampled on August 11, 1989. The field produces 28-30° gravity oil, by waterflood recovery. Four samples were obtained, as outlined below.

Ventura				air temp	source temp
OF-50	tank	bag valve	100 well composite	25º C	40° C
OF-51	well L-131	bag valve	casing gas	22º C	27° C
OF-52	vapor recovery	canister direct	field composite	27º C	41° C
OF-53	vapor recovery	canister direct	shipping tank	30° C	35° C

6. Wilmington Field

Sampling was conducted at THUMS Pier J location on August 28, 1989 A secondary sump was sampled here, using the flux chamber described earlier. The pontoon system was not used. A 4' x 8' section of the sump covering was removed, and the flux chamber was lowered to the surface with a rope. Four samples were obtained at this location, as shown below. Average field gravity was 17.5° API.

Wilmington				air temp	source temp
OF-60	Pier J sump	flux chamber		18º C	34º C
OF-61	tank TK 003	headspace	roof hatch	24º C	37° C
OF-62	FWKO tank #3	canister direct	_	23º C	26º C
OF-63	well J-341	bag valve	casing gas	24º C	26º C

7. West Coyote Field

Sampling was conducted on August 28, 1989. This field produces crude oil in the 26-30° gravity range. Waterflood is the method of recovery. No heat treating is performed at this facility. Four samples were obtained, as shown below.

West Coyote				air temp	source temp
OF-70	AWT tank 105	bag valve	·	30° C	32º C
OF-71	work tank #1	headspace	roof vent	34º C	40° C
OF-72	stock tank	bag port	manometer port	34º C	34º C
OF-73	vapor recovery	bag valve	field vapor recovery	31º C	32º C

8. Other

The Union Oil HS&P facility supporting Platform Irene production was visited on May 19, 1989. This facility was recently built, and contains state-of-the-art emission controls. No readily accessible sampling points were available. This facility was not sampled.

On June 2, 1989, the San Ardo field was visited. A facility tour was conducted, and revealed very high H₂S concentrations (in excess of 10,000 PPM) at most sampling locations. The operators (Texaco) indicated that self-contained breathing apparatus (SCBA) would be required for sampling. This site was omitted from further consideration. The Cat Canyon field satisfied the Coastal Crude sampling requirements.

G. Format For Results

The analytical results are reported in a format illustrated by Table 6. The concentrations of all integrated peaks in the original sample were initially converted to mg/m3. These concentrations were summed with the methane concentration (expressed in mg/m3) and results were converted to a percentage of this total (expressed as % by mass). For most samples, the high resolution capillary column provided as many as several hundred resolvable peaks, as shown in Figure 18. Not all of these peaks could be positively identified. To aid in interpretation, each chromatogram was divided into regions bounded by a normal hydrocarbon, as shown in Figure 19. This

classification scheme results in assigning all unknown peaks as Cn if they appear between normal Cn and Cn+1 hydrocarbons. By this method, C5 hydrocarbons are defined as having retention times between n-pentane and n-hexane. Another way of looking at this classification is based on the Kovats Retention Index (KRI). A compound listed as "OTHER Cn" will have a KRI between 100*n and 100*(n+1). Those chromatographic peaks which could not be positively identified were placed in a carbon number category by this method. It is important to note that these are operational definitions, and do not represent the actual number of carbon atoms in a given component. Branching of a hydrocarbon tends to make it more volatile than its straight-chain homolog. Thus, unidentified branched hydrocarbons with n carbons will usually be assigned to the Cn-1 carbon range.

Table 6	. Format	for C)ii l	Field	Results
Taule 0	. I Ommat	TOT (/11 ·	1 1010	IVOSUID

Table 6- Format for Oil Field	Results
	OF-63
Methane Ethane Propane i-Butane n-Butane 2,2-dimethylpropane i-Pentane	9.3724 8.6278 3.7709 7.6645 14.2861 0.1059 8.6462
n-Pentane 2,2-Dimethylbutane Cyclopentane 2,3-Dimethylbutane 2-Methylpentane 3-Methylpentane	5.4645 0.1539 0.5612 0.0000 2.6425 1.9294
n-Hexane Methylcyclopentane 2,4-Dimethylpentane Benzene Cyclohexane 2-Methylhexane 2,3-Dimethylpentane 3-Methylhexane	1.9154 3.1383 0.1542 0.5559 0.0316 0.5707 0.5102 0.8294
n-Heptane Methylcyclohexane 2,4-Dimethylhexane 2,3,4-Trimethylpentane Toluene 2,3-Dimethylhexane 2-Methylheptane 3-Ethylhexane	1.0401 2.0397 0.1030 0.0523 0.1805 0.0840 0.6672 0.3136
n-Octane Ethylbenzene p-Xylene m-Xylene o-Xylene	0.6727 0.5052 0.0000 0.5832 0.2485
n-Nonane i-Propylbenzene n-Propylbenzene 3-Ethyltoluene 1,3,5-Trimethylbenzene 2-Ethyltoluene t-butylbenzene 1,2,4-Trimethylbenzene i-butylbenzene s-butylbenzene	0.3525 0.0516 0.1527 0.1630 0.1066 0.0694 0.0000 0.2217 0.0500 0.0608
n-Decane 1,2,3-Trimethylbenzene 1,3-Diethylbenzene 1,4-Diethylbenzene n-butylbenzene 1,2-diethylbenzene	0.0000 0.1393 0.0486 0.0457 0.0000 0.0000
n-undecane Other C4 Other C5 Other C6 Other C7 Other C8 Other C9 Other C10	0.0000 0.0000 0.9634 5.6426 5.4870 5.4826 2.7415 0.6598
Other C11	0.1404

H. Results

Hydrocarbon speciation information is arranged by oil field. Tables 7 through 13 contain results for all samples listed in Table 6. Additionally, these data were organized into a LOTUS 1-2-3 database. The format of the database is actually the transpose of the results shown in Tables 7-13. Compound names are column headings (fields), and sample numbers are rows (records). A portion of the database is shown in Table 14. A copy of the database, named OF_SUMRY.WK1, was copied to a 3.5 inch floppy disk, and sent to ARB along with this report.

Figure 18- Representative Chromatogram

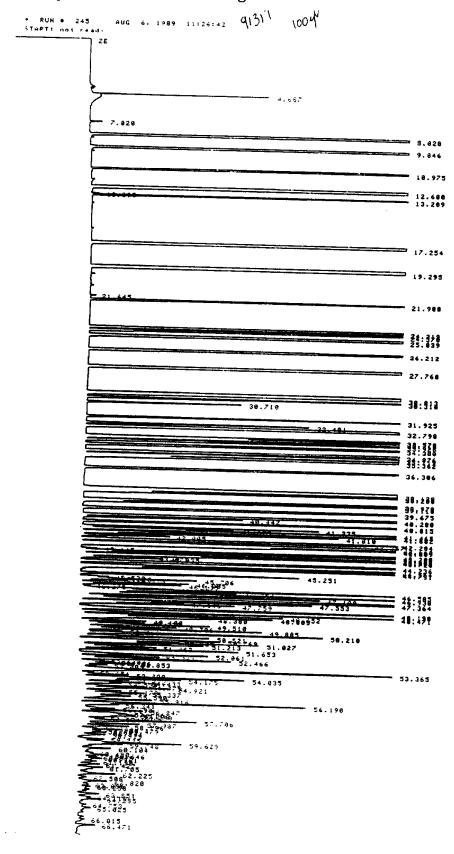


Figure 19 - Hydrocarbon Classification by Carbon Number

						٠
	TIMETABLE S	TOP				
	Error stori	ne sienal	to 1	1:SIGHAL	. BNC	
	ATTEMPTED W	RITE PAST	FNO	05 575		
	RUN# 176	J	UL	18, 1989	08:53:33	
-	AREA% RT	APFA TY	PE	WIDTH '	AREAZ	
	9.307	528	٧P	. 953	. 15155	
	12:054	645	0			
	21.567	1875	<u>, e v</u>	.048	.53817	
بيد ن	24-438بها 32-467	1846			29050	
7	38.835	1261	8 P	. 963	.36194	
	38.882	581	PV	. 069	.16676	
_	39.416	3179	8 P	.069 .075	.91244 .18 0 25	
C	7 48.211	628 807	V V	. 869	. 23163	
	42.180	559	PV	. 998	. 16943	
	42.295	2984	vv	. 968	.83351	
	42.548	890	VV	.067	. 25545	
	43.868	- 338	80	967	23745	n-octane
	44.384	2530	PV	.067 .069	.72617	
	45.019 45.301	873	vv	. 098	,25057	
- 1	45.479	1953	٧v	. 079	.56855	
	45.668	925	VV	.078	. 26550	
	46.409	917	VV	. 115	.26320 .24770	
j	46.593 46.834	863 1383	V V	. 879 . 874	.37399	
_	47 001	1937	VV	.080	. 55596	
Cg	47.296	1757	VV	. 082	.50438	
1	47.516	1286	VP	. 081	.36911	
į	47.864 48.212	585 	BH HH	. 875 080	.16791 1.50084	57.11 A
	46.408	832	нн	. 107	. 23889	ETY!
- 1	49.082	1594	нн	. 896	.45751	
	49.194	1239	нн	. 890	.35562	•
	49.537 49.820	2624 534	HH	.095 .096	.75315 .15327	
}	49.984	2571	нн	. 107	.73793	
- 1	50.245	2003	нн	. 115	.57491	
.	50.505	2942	нн	.137	.58610	
	50.680 50.926	1626 (5369)	нн	.081	.48105 1.54162	
ŀ	51.183	664	нн	. 071	.19858	(11192)
- *		1056	-++-	+127	- 53271	
ſ	51.731	2255	нн	.081	.64724	
	51.815	3783	нн		1.06294	
	52.805 52.239	6078	нн	.112	.46268 1.74452	
	52.637	1438	нн	. 099	.41274	
_]	53.009	2926	нн	. 103	. 83983	
ζġ	53.118	4369	нн	. 138	1.25400	
i	53.405 53.526	813 <u>2</u> 925	нн	.087 .114	.23335 .83954	
	53.741	7882	нн	.131	2.26231	
. 1	54.022	3077	нн	. 094	1.45721	
4	54.186	3848	нн	. 104	1.10446	
1	54.288	2504	нн	. 892	.71878	
1	54.525 54.648	2335 1880	HH	.102	.67020 .53960	
1	54.958	3235	нн	. 168	.92852	
ĺ	55.111	2215	нн	.116	.63575	

Data Summaries Follow

racio / - Rom River Summary	1194100	aroon spe	cies by 70 i	*1a33		
	OF-01	OF-02	OF-03	OF-04	OF-05	OF-06
Methane	0.1616	81.3998	62.0949	60.7789	95.9289	4.4862
Ethane	0.0931	0.1565	0.1214	1.3946	0.2717	0.4191
Propane	0.1499	0.0955	0.0781	0.3922	0.0716	0.3025
i-Butane	0.0000	0.0647	0.0531	0.1601	0.0542	0.3003
n-Butane	0.1825	0.0842	0.0684	0.0914	0.0352	0.2139
2,2-dimethylpropane	0.0000	0.3083	0.2510			
i-Pentane				0.6376	0.1440	0.3897
i-remane	0.0000	0.1803	0.1558	0.1549	0.0434	0.4758
n-Pentane	0.0000	0.0321	0.0250	0.0234	0.0066	0.0696
2,2-Dimethylbutane	0.5323	0.3794	0.3487	0.2715	0.0599	0.9194
Cyclopentane	0.0000	0.0000	0.0000	0.0000	0.1704	0.0000
2,3-Dimethylbutane	0.3055	1.3302	1.2881	0.8293	0.0000	2.9941
2-Methylpentane	0.0000	0.0203	0.0174	0.0025	0.0000	0.0637
3-Methylpentane	0.0000	0.0737	0.0712	0.0696	0.0093	0.2005
3-Mothy pontane	0.0000	0.0757	0.0712	0.0090	0.0093	0.2003
n-Hexane	0.0724	0.0194	0.0082	0.3656	0.0000	0.0370
Methylcyclopentane	0.0000	0.0121	0.1412	0.0153	0.0000	0.3065
2,4-Dimethylpentane	0.0931	0.2317	0.2654	0.1847	0.0341	0.6060
Benzene	0.1318	0.0137	0.0000	0.2571	0.0000	0.0177
Cyclohexane	0.0000	0.1322	0.1564	0.1040	0.0000	0.3697
2-Methylhexane	0.2952	0.6399	0.7923	0.4250	0.0902	0.0281
2,3-Dimethylpentane	0.0000	0.0000	0.0000			
2 Mathylhavona	0.0000			0.0338	0.0088	2.0899
3-Methylhexane	0.0000	0.0223	0.0228	0.0332	0.0000	0.0844
n-Heptane	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Methylcyclohexane	0.0000	0.0158	0.0169	0.0162	0.0000	0.1434
2,4-Dimethylhexane	0.1649	0.1780	0.2580	0.1924	0.0000	0.6607
2,3,4-Trimethylpentane	0.2291	0.1985	0.2951	0.2434	0.0341	0.6631
Toluene	0.1059	0.0800				
			0.1192	0.1048	0.0141	0.2593
2,3-Dimethylhexane	0.0000	0.0466	0.0566	0.1007	0.0170	0.1882
2-Methylheptane	0.0000	0.0298	0.0513	0.0196	0.0115	0.0592
3-Ethylhexane	0.1587	0.1108	0.1775	0.9907	0.0154	0.5925
n-Octane	1.6531	0.8900	1.4281	1.1606	0.0000	1.2543
Ethylbenzene	1.4534	0.4798	0.7963	0.6379	0.1166	0.4558
p-Xylene	0.0384	0.0155	0.0250	0.0187	0.0000	0.1605
m-Xylene	0.0573	0.0091	0.0096	0.0393	0.0000	0.0462
o-Xylene	0.5676	0.1397	0.2040	0.2463	0.0432	0.8641
n-Nonane	0.5269	0.0804				
		-	0.1463	0.0154	0.0000	0.7433
i-Propylbenzene	0.3997	0.0751	0.1261	0.0649	0.0157	0.2696
n-Propylbenzene	0.5226	0.0704	0.1432	0.2459	0.0000	0.5119
3-Ethyltoluene	0.6157	0.0754	0.0701	0.3010	0.0459	0.2927
1,3,5-Trimethylbenzene	1.1485	0.1059	0.2325	0.3917	0.0460	0.6053
2-Ethyltoluene	1.0170	0.1053	0.2072	0.4058	0.0187	0.6919
t-butylbenzene	1.4128	0.1515	0.2642	0.2284	0.0781	0.6499
1,2,4-Trimethylbenzene	1.8178	0.1777	0.3203	0.0673	0.0000	0.1576
i-butylbenzene	0.6893	0.0000	0.0000	0.4387	0.0000	0.0000
s-butylbenzene	1.5427	0.1154	0.2455	0.0827	0.0000	0.4963
n-Decane	0.9377	0.0767	0.1528	0.0000	0.0255	0.3824
1,2,3-Trimethylbenzene						
1,3-Diethylbenzene	1.2611	0.1167	0.2233	0.3045	0.0485	0.5393
	1.5037	0.0883	0.2133	0.3182	0.0000	0.3418
1,4-Diethylbenzene	1.2994	0.0874	0.2261	0.2255	0.0212	0.3497
n-butylbenzene	1.0621	0.0273	0.1696	0.0000	0.0000	0.1890
1,2-diethylbenzene	0.9061	0.0729	0.1544	0.2284	0.0121	0.4960
n-undecane	0.0000	0.0000	0.1151	0.0000	0.0000	0.0089
Other C4	0.0000	0.0000	0.0000	0.1460	0.0000	0.0000
Other C5	0.0000	0.0000	0.0000	0.0566	0.0000	0.0000
Other C6	0.0000	0.6617	0.7074	0.6329	0.0000	3.0064
Other C7	2.7537	2.7837	4.5832	2.6022	0.4848	21.5246
Other C8	9.6620	3.1244	5.1639	5.9405	0.7901	22.4750
Other C9	24.3261	2.7101	5.6391	10.3142	0.8362	19.7780
Other C10	30.0711	1.8284	6.0923	6.6704	0.3693	6.7337
Other C11	10.0782	0.0751	5.4074	0.3234	0.0275	0.0353

Table 8 - Elk Hills Summary	Hydrod	arbon Spe	cies by % N	Mass				
	OF-10	OF-11	OF-12	OF-13	OF-14	OF-15	OF-16	OF-17
Methane	44.8895	37.7408	33.4312	11.8005	31.9680	19.4226	35.1586	26.7810
Ethane	7.9019	7.6800	12.7717	9.5479	15.4250	8.4997	3.7104	7.5402
Propane i-Butane	13.0885 3.1748	14.8836 3.3993	17.2663 3.4171	17.0718 5.7194	17.7471 3.8778	15.3786 4.2802	12.6201 3.2037	14.1825 5.0340
n-Butane	10.3318	6.7414	10.8072	17.3072	11.4358	3.3683	15.2084	13.2046
2,2-dimethylpropane	0.1106	0.1170	0.1195	0.0427	0.1169	0.6509	0.1633	0.0420
i-Pentane	2.8767	1.5246	3.3797	2.0964	3.6524	1.6843	1.8193	4.4784
n-Pentane 2,2-Dimethylbutane	2.7182 0.1824	1.4220	3.3991	3.2146	3.4792	1.5078	3.5079	3.0220
Cyclopentane	0.1824	0.1976 0.4740	0.1976 0.4656	0.0925 0.2939	0.1790 0.4103	0.0966 0.1599	0.3145 0.7297	0.0877 0.2727
2,3-Dimethylbutane	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2-Methylpentane	1.0121	1.1492	0.9909	1.7049	0.9906	1.0162	0.5465	1.2021
3-Methylpentane	0.6783	0.7795	0.6824	1.6037	0.1099	0.0000	0.4636	1.4428
n-Hexane Methylcyclopentane	1.0797 1.5561	1.2686 1.9090	1.0330 1.7244	3.2012 2.7693	0.9704	2.4788	0.8823	2.3533
2,4-Dimethylpentane	0.0000	0.1213	0.1125	0.0910	1.5368 0.0928	1.4020 0.0923	3.0811 0.1934	2.4687 0.0791
Benzene	0.0799	0.0912	0.0694	0.4320	0.0674	0.4661	0.0287	0.2989
Cyclohexane	0.0255	0.0307	0.0293	0.0000	0.0237	0.0177	0.0486	0.0164
2-Methylhexane	0.2065	0.2603	0.2276	0.4923	0.1838	0.4907	0.1631	0.3990
2,3-Dimethylpentane 3-Methylhexane	0.2107 0.2814	0.2603 0.3573	0.2397 0.2411	0.2208 0.6209	0.1905 0.2522	0.2270	0.4335	0.1875
n-Heptane	0.3279	0.4367	0.3039	1.0452	0.2522	0.0000	0.3197 0.1562	0.5050
Methylcyclohexane	0.8685	1.1612	1.0033	1.3402	0.7933	1.0439 1.3160	2.2377	0.7316 1.1241
2,4-Dimethylhexane	0.1520	0.0000	0.0000	0.0000	0.0000	0.0000	0.0851	0.1298
2,3,4-Trimethylpentane	0.3075	0.0000	0.3843	0.0000	0.0343	0.0163	0.0302	0.0124
Toluene	0.1012	0.1382	0.0864	0.4755	0.0771	0.4887	0.0738	0.2453
2,3-Dimethylhexane 2-Methylheptane	0.0000 0.0924	0.0323 0.1416	0.0273 0.0945	0.0257 0.0000	0.0000 0.0185	0.0277 0.0000	0.0548 0.0000	0.0197
3-Ethylhexane	0.0000	0.0825	0.0333	0.0000	0.0183	0.1267	0.0000	0.1889 0.0000
n-Octane	0.1923	0.3093	0.2305	0.2394	0.1645	0.2901	0.3371	0.1331
Ethylbenzene	0.0741	0.1219	0.0938	0.0619	0.0506	0.0976	0.2080	0.0386
p-Xylene m-Xylene	0.0195 0.0311	0.0545 0.0333	0.0310 0.0210	0.0306 0.1080	0.0207 0.0302	0.0520	0.0467	0.0208
o-Xylene	0.0221	0.0333	0.0210	0.1030	0.0302	0.1659 0.0545	0.0572 0.0504	0.0462 0.0160
n-Nonane	0.0260	0.0241	0.0186	0.0471	0.0281	0.0931	0.0408	0.0210
i-Propylbenzene	0.0078	0.0000	0.0034	0.0000	0.0045	0.0071	0.0000	0.0000
n-Propylbenzene 3-Ethyltoluene	0.0190 0.0169	0.0138	0.0110	0.0000	0.0125	0.0177	0.0000	0.0000
1,3,5-Trimethylbenzene	0.0137	0.0107 0.0000	0.0093 0.0000	0.0000	0.0050 0.0092	0.0000	0.0000	0.0000
2-Ethyltoluene	0.0000	0.0097	0.0087	0.0000	0.0066	0.0000	0.0000	0.0000
t-butylbenzene	0.0000	0.0115	0.0101	0.0000	0.0000	0.0000	0.0000	0.0000
1,2,4-Trimethylbenzene	0.0350 0.0000	0.0000	0.0055	0.0000	0.0000	0.0381	0.0000	0.0000
i-butylbenzene s-butylbenzene	0.0000	0.0000 0.0072	0.0049 0.0000	0.0000	0.0000	0.0000	0.0000	0.0000 0.0000
n-Decane	0.0075	0.0094	0.0064	0.0000	0.0041	0.0194	0.0451	0.0000
1,2,3-Trimethylbenzene	0.0289	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1,3-Diethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1,4-Diethylbenzene n-butylbenzene	0.0000 0.0000	0.0000 0.0000	0.0000 0.0000	0.0000	0.0000 0.0000	0.0000	0.0000	0.0000
1,2-diethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0380	0.0000	0.0000 0.0000
n-undecane	0.0065	0.0000	0.0000	0.0000	0.0092	0.0000	0.0000	0.0000
Other C4	0.5783	6.1069	0.0000	5.2441	0.0577	13.7463	0.0000	2.5913
Other C5	1.4612	3.0812	0.7107	6.5695	1.3404	9.1198	1.2993	6.2761
Other C6	2.2153	3.3493	3.1000	3.6424	1.9094	6.4305	6.2250	3.0361
Other C7 Other C8	1.3296 0.7813	2.3796	1.5896	2.0599	1.3557	4.3198	3.7814	1.2699
Other C9	0.7813	1.3165 0.6090	1.0459 0.4462	0.6321 0.1228	0.6379 0.2824	0.9180 0.3332	1.99 7 9 0.6220	0.4258 0.0753
Other C10	0.1121	0.1073	0.0851	0.0000	0.2824	0.0000	0.0220	0.0733
Other C11	0.0219	0.0068	0.0040	0.0000	0.0098	0.0000	0.0000	0.0000

Table 9 - Belridge Summary	Hydrod	arbon Spe	cies by % N	Mass				
	OF-20	OF-21	OF-22	OF-23	OF-24	OF-25	OF-26	OF-27
Methane	0.6309	47.8262	44.8636	45.7334	25.6069	2.7544	95.9626	98.1996
Ethane	13.8534	10.1622	6.8113	9.2589	7.9440	5.4703	0.5781	0.6958
Propane	20.3860	13.5873	10.3987	13.3879	16.7611	4.5376	0.1836	0.1861
i-Butane n-Butane	1.9291 17.5464	2.7121	2.5031	3.0755	4.2843	2.1106	0.0375	0.0213
2,2-dimethylpropane	0.0456	7.7710 0.0203	8.2760 0.0185	9.7694	14.0011	6.6176	0.1228	0.0335
i-Pentane	5.9460	2.9425	3.5109	0.0251 3.7319	0.0415 5.0878	0.2065 5.3812	0.0794	0.0554
					3.0076		0.0535	0.0080
n-Pentane	8.3204	3.3931	3.9112	3.8510	5.6848	4.3558	0.0456	0.0079
2,2-Dimethylbutane	0.0964	0.0438	0.0407	0.0409	0.0828	0.2502	0.0000	0.0050
Cyclopentane	0.0000	0.0000	0.1801	0.1537	0.2917	0.6577	0.0000	0.0000
2,3-Dimethylbutane 2-Methylpentane	0.3293 1.7627	0.1474 1.0353	0.0000 1.3757	0.0000	0.0000	0.0000	0.0191	0.0011
3-Methylpentane	1.6061	0.6445	0.9477	1.1674 0.7538	1.0834 1.0913	2.1277 1.4123	0.0223 0.0000	0.0031 0.0000
n-Hexane	3.0647	1.1569	1.5742	1.1753	1.9673	2.3156	0.0206	0.0038
Methylcyclopentane	3.4631	0.0164	0.0160	0.0137	2.8540	2.5628	0.0057	0.0000
2,4-Dimethylpentane	0.1121	0.0442	0.0595	0.0414	0.0880	0.2350	0.0000	0.0000
Benzene	0.3862	0.1231	0.0872	0.0919	0.1998	0.2686	0.0000	0.0050
Cyclohexane	0.0219	0.0085	0.0109	0.0075	0.0177	0.0000	0.0000	0.0000
2-Methylhexane	0.5507	0.1767	0.3242	0.0000	0.3533	0.6553	0.0000	0.0000
2,3-Dimethylpentane 3-Methylhexane	0.3258 0.0000	0.1429 0.2271	0.2174 0.4621	0.2020 0.2817	0.2560 0.4480	0.9489 0.9310	0.0051 0.0000	0.0000
n-Heptane	1.2952	0.3164	0.7085	0.3518	0.7147	1.3600	0.0000	0.0009
Methylcyclohexane	0.1831	0.0000	0.0000	0.0840	0.0000	0.4621	0.0000	0.0003
2,4-Dimethylhexane	0.0550	0.1227	0.0364	0.1121	0.0376	0.2385	0.0061	0.0000
2,3,4-Trimethylpentane	0.0309	0.2526	0.5542	0.2322	0.0216	0.3665	0.0799	0.0027
Toluene	0.5882	0.0236	0.3102	0.1370	0.3313	0.4900	0.0000	0.0038
2,3-Dimethylhexane	0.0456	0.0175	0.0310	0.0137	0.0275	0.1998	0.0000	0.0000
2-Methylheptane	0.4294	0.0236	0.0439	0.0197	0.2050	0.7450	0.0078	0.0000
3-Ethylhexane	0.1786	0.0477	0.1203	0.0482	0.0935	0.3599	0.0000	0.0000
n-Octane	0.4324	0.0814	0.0870	0.0351	0.0874	1.3665	0.0088	0.0039
Ethylbenzene	0.1841	0.0755	0.1553	0.0472	0.0741	1.0917	0.0145	0.0051
p-Xylene	0.0000	0.0045	0.1452	0.0592	0.0000	0.2763	0.0000	0.0046
m-Xylene	0.2260	0.0334	0.0765	0.0250	0.0839	0.4733	0.0000	0.0000
o-Xylene	0.0891	0.0056	0.0552	0.0220	0.0280	0.2783	0.0057	0.0035
n-Nonane	0.1393	0.0186	0.0203	0.0370	0.0201	0.2195	0.0095	0.0074
i-Propylbenzene	0.0000	0.0027	0.0034	0.0025	0.0039	0.0743	0.0000	0.0000
n-Propylbenzene	0.0345	0.0234	0.0283	0.0061	0.0094	0.4000	0.0092	0.0064
3-Ethyltoluene	0.0133	0.0072	0.0116	0.0000	0.0093	0.2899	0.0211	0.0097
1,3,5-Trimethylbenzene 2-Ethyltoluene	0.0269 0.0258	0.0057 0.0026	0.0187 0.0182	0.0041 0.0038	0.0000 0.0036	0.0000 0.1688	0.0186	0.0116
t-butylbenzene	0.0238	0.0020	0.0132	0.0000	0.0000	0.1000	0.0118 0.0000	0.0158 0.0000
1,2,4-Trimethylbenzene	0.0066	0.0048	0.0046	0.0164	0.0042	0.4794	0.0000	0.0000
i-butylbenzene	0.0058	0.0000	0.0042	0.0000	0.0000	0.0605	0.0101	0.0000
s-butylbenzene	0.0074	0.0045	0.0045	0.0000	0.0021	0.0878	0.0000	0.0000
n-Decane	0.0057	0.0011	0.0290	0.0112	0.0000	0.0599	0.0184	0.0244
1,2,3-Trimethylbenzene	0.0054	0.0000	0.0000	0.0000	0.0051	0.0000	0.0490	0.0057
1,3-Diethylbenzene	0.0128	0.0000	0.0064	0.0000	0.0000	0.2104	0.0000	0.0015
1,4-Diethylbenzene	0.0000	0.0042	0.0095	0.0000	0.0038	0.2106	0.0192	0.0225
n-butylbenzene	0.0078	0.0057	0.0049	0.0020	0.0000	0.0000	0.0000	0.0203
1,2-diethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0041
n-undecane	0.0000	0.0000	0.0093	0.0000	0.0000	0.0999	0.0219	0.0000
Other C4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Other C5	2.8126	0.0000	0.6376	0.5484	1.6789	1.3806	0.0553	0.0126
Other C6	6.9258	0.5288	5.9315	3.7219	4.2202	8.7054	0.0935	0.0171
Other C7 Other C8	3.0713	3.6994	2.9653	1.0916	3.0840	15.5060	0.1773	0.0106
Other C9	1.8956 0.7019	1.4513 0.9881	1.6682 0.6194	0.4752 0.0943	0.9441 0.1285	11.9369	0.6540	0.0655
Other C10	0.7019	0.9881	0.0174	0.0343	0.1283	6.6643 1.3815	0.8882 0.5560	0.2110 0.2885
Other C11	0.0394	0.0092	0.0018	0.0056	0.0000	0.3470	0.3300	0.2000

Table 10 - Cat Canyon Summary Hydrocarbon Species by % Mass

OF-40	OF-41	OF-42	OF-43	OF-44	
Methane	40.6929	10.0741	8.0981	0.0000	0.0000
Ethane	8.8839	20.1940	1.5655	1.6118	0.0000
Propane	14.1404	11.3004	4.9484	1.3702	0.0000
i-Butane	3.1034	1.5022	4.5482	0.0000	1.0505
n-Butane	8.2204	4.4444	16.7562	2.4984	0.0000
2,2-dimethylpropane	0.0114	0.0000	0.0443	0.0000	0.0000
i-Pentane	2.8269	1.6489	18.5162	3.5461	4.3902
n-Pentane	0.8501	1.6241	18.2855	4.3522	5.2835
2,2-Dimethylbutane	0.0000	0.0000	0.0000	0.0000	0.0000
Cyclopentane	0.2525	0.1323	0.0000	0.0000	1.0410
2,3-Dimethylbutane	0.0000	0.0000	0.0000	0.0000	0.0000
2-Methylpentane	1.5351	0.6920	5.8657	4.0751	6.1335
3-Methylpentane	1.1323	0.6022	3.7394	0.0000	4.9084
n-Hexane	1.7048	0.9060	4.8494	5.7627	6.6935
Methylcyclopentane	1.1296	1.2395	2.9251	5.2924	5.9473
2,4-Dimethylpentane	0.0375	0.0000	0.0000	0.0000	0.0000
Benzene	0.2509	1.8187	0.3463	9.1484	10.7339
Cyclohexane	0.0000	0.0000	0.0122	0.0000	0.0000
2-Methylhexane	0.3618	0.2747	0.5003	0.0000	1.6592
2,3-Dimethylpentane	0.2302	0.1935	0.3006	0.0000	1.3305
3-Methylhexane	0.6061	0.5048	0.6828	0.0000	2.7133
n-Heptane	0.9354	0.9240	0.7250	5.2258	3.2642
Methylcyclohexane	0.6467	1.0305	0.5577	5.5640	3.2339
2,4-Dimethylhexane	0.0000	0.0461	0.0000	0.0000	1.0936
2,3,4-Trimethylpentane	0.0155	0.0000	0.0075	0.0000	0.0000
Toluene	0.4204	2.8143	0.1548	10.4338	6.7816
2,3-Dimethylhexane	0.0453	0.0744	0.0159	0.0000	0.0000
2-Methylheptane	0.3968	0.6905	0.0994	0.0000	0.0000
3-Ethylhexane	0.1649	0.3057	0.0108	0.0000	0.7464
n-Octane	0.4462	1.1482	0.0601	4.3452	1.8149
Ethylbenzene	0.1989	1.2698	0.0247	4.5312	1.9672
p-Xylene	0.0800	0.3562	0.0077	4.9276	0.6668
m-Xylene	0.1463	1.0711	0.0126	0.0000	1.6627
o-Xylene	0.0813	0.7089	0.0080	4.5835	1.2487
n-Nonane	0.1951	1.5824	0.0082	4.1871	1.1148
i-Propylbenzene	0.0183	0.1644	0.0000	0.0000	0.0000
n-Propylbenzene	0.0456	0.5008	0.0000	0.0000	0.0000
3-Ethyltoluene	0.0446	0.5516	0.0000	0.0000	0.0000
1,3,5-Trimethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000
2-Ethyltoluene	0.0000	0.1692	0.0000	0.0000	0.0000
t-butylbenzene 1,2,4-Trimethylbenzene	0.0337 0.0473	0.2522 0.6815	0.0000	0.0000 4.9369	0.0000
i-butylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000
s-butylbenzene	0.0000	0.2217	0.0000	0.0000	0.0000
n-Decane	0.0060	0.0694	0.0000	0.0000	0.0000
1,2,3-Trimethylbenzene	0.0299	0.3868	0.0000	0.0000	0.0000
1,3-Diethylbenzene	0.0246	0.4904	0.0000	0.0000	0.0000
1,4-Diethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000
n-butylbenzene	0.0000	0.1752	0.0000	0.0000	0.0000
1,2-diethylbenzene	0.0000	0.0000	0.0000	0.0000	0.0000
n-undecane	0.0000	1.2176	0.0000	0.0000	0.0000
Other C4					
	1.1117	0.0000	0.0000	0.0000	0.0000
Other C5 Other C6	3.3706 1.6494	0.6062 2.0726	2.7335 2.6472	0.0000	1.3944
Other C7	1.3692	2.0726 2.4995	2.6472 0.8324	0.0000	9.5263 5.7191
Other C8	1.3995	5.4748	0.8324	5.4339	4.5759
Other C9	0.6859	8.4377	0.0393	3.4339 8.1739	1.7149
Other C10	0.3521	5.1144	0.0000	0.0000	1.7149
Other C11	0.0684	1.7402	0.0000	0.0000	0.0000
	J.JUU-T	2.7 702	5.5550	5.5550	5.5500

Table 11 - Ventura Field Sumr	Hydrocarbon Species by % Mass						
	OF-5 0	OF-51	OF-52	OF-53			
Methane	26.3353	24.7704	12.8696	69.8572			
Ethane	6.4585	7.5008	6.8363	9.0459			
Propane	18.9621	23.1831	25.1314	4.9068			
i-Butane	6.0712	7.6461	7.9999	0.6395			
n-Butane	14.4739	16.1895	19.0352	2.1218			
2,2-dimethylpropane	0.0146	0.0162	0.0190	0.0000			
i-Pentane	5.8607	5.7925	6.7579	2.5646			
n-Pentane	5.1406	4.6708	5.8342	2.6707			
2,2-Dimethylbutane	0.0000	0.0520	0.0000	0.0235			
Cyclopentane	0.0000	0.0000	0.0000	0.4227			
2,3-Dimethylbutane	1.5218 0.0000	1.1875 0.0071	0.0000	0.0000			
2-Methylpentane 3-Methylpentane	0.0000	0.8659	0.0000 1.0630	0.0000 0.0000			
· •							
n-Hexane	1.5428	1.1171	1.4054	0.6655			
Methylcyclopentane	1.9954	1.2884	1.8668	0.8751			
2,4-Dimethylpentane Benzene	0.0469 0.1318	0.0325	0.0415	0.0192			
Cyclohexane	0.1318	0.3128 0.0000	0.1360 0.0052	0.0970 0.0000			
2-Methylhexane	0.2858	0.1599	0.2234	0.0000			
2,3-Dimethylpentane	0.1590	0.0843	0.1171	0.0514			
3-Methylhexane	0.4622	0.2371	0.3428	0.1400			
n-Heptane	0.6540	0.2606	0.4833	0.1851			
Methylcyclohexane	0.8599	0.2270	0.6997	0.2890			
2,4-Dimethylhexane	0.0282	0.0087	0.0000	0.0000			
2,3,4-Trimethylpentane	0.0126	0.0000	0.0084	0.0000			
Toluene	0.2022	0.2009	0.1689	0.1034			
2,3-Dimethylhexane	0.0253	0.0071	0.0153	0.0000			
2-Methylheptane	0.0378	0.0000	0.1659	0.0795			
3-Ethylhexane	0.1086	0.0000	0.0819	0.0000			
n-Octane	0.2432	0.0797	0.1575	0.0881			
Ethylbenzene	0.1134	0.0976	0.0743	0.0492			
p-Xylene	0.0620	0.0787	0.0368	0.0336			
m-Xylene	0.0950	0.0000	0.0745	0.0652			
o-Xylene	0.0467	0.0461	0.0341	0.0502			
n-Nonane	0.1024	0.0383	0.0606	0.0629			
i-Propylbenzene	0.0078	0.0000	0.0000	0.0000			
n-Propylbenzene	0.0229	0.0174	0.0000	0.0191			
3-Ethyltoluene 1,3,5-Trimethylbenzene	0.0000	0.0000	0.0166	0.0000			
2-Ethyltoluene	0.0199 0.0093	0.0000	0.0000	0.0000			
t-butylbenzene	0.0053	0.0000	0.0062	0.0000			
1,2,4-Trimethylbenzene	0.0351	0.0000	0.0002	0.0000			
i-butylbenzene	0.0000	0.0000	0.0000	0.0138			
s-butylbenzene	0.0000	0.0000	0.0000	0.0178			
n-Decane	0.0196	0.0000	0.0000	0.0100			
1,2,3-Trimethylbenzene	0.0068	0.0000	0.0000	0.0539			
1,3-Diethylbenzene	0.0000	0.0000	0.0000	0.0259			
1,4-Diethylbenzene	0.0000	0.0000	0.0000	0.0000			
n-butylbenzene	0.0000	0.0000	0.0000	0.0000			
1,2-diethylbenzene	0.0000	0.0000	0.0000	0.0000			
n-undecane	0.0205	0.0000	0.0000	0.0000			
Other C4	0.0000	0.0246	0.0060	0.0000			
Other C5	2.0335	1.4400	2.4045	1.3762			
Other C7	2.4888	1.2186	3.7835	0.9365			
Other C7 Other C8	1.7315 0.9871	0.5669	1.0877	0.6074			
Other C9	0.9871	0.3069 0.2100	0.5952 0.2615	0.5527 0.8476			
Other C10	0.4312	0.2100	0.2513	0.3196			
Other C11	0.0056	0.0000	0.0123	0.0092			
	0.0000	3.3000	U.V.123	3.0072			

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Table 12 - Wilmington Field S	Summary	Hydrocarbon Species by % Mass					
	OF-60	OF-61	OF-62	OF-63			
Methane	0.0000	69.7258	86.2213	9.3724			
Ethane	0.2429	3.4827	2.5933	8.6278			
Propane	0.8504	3.9190	1.9722	3.7709			
i-Butane	0.8152	2.2601	1.6328	7.6645			
n-Butane	2.1302	3.9861	1.9669	14.2861			
2,2-dimethylpropane	0.0220	0.0256	0.0258	0.1059			
i-Pentane	2.2168	2.5187	1.1618	8.6462			
n-Pentane	2.2614	1.9546	0.7548	5.4645			
2,2-Dimethylbutane	0.0338	0.0604	0.0351	0.1539			
Cyclopentane	0.4349	0.0000	0.0000	0.5612			
2,3-Dimethylbutane	0.3434	0.2522	0.1145	0.0000			
2-Methylpentane 3-Methylpentane	1.2635 1.0717	0.8062 0.6593	0.2607 0.2066	2.6425 1.9294			
3-Methylpentalie	1.0717			1.7274			
n-Hexane	1.3441	0.6473	0.1832	1.9154			
Methylcyclopentane	2.5612	0.0000	0.3367	3.1383			
2,4-Dimethylpentane	0.1425	0.0687	0.0243	0.1542			
Benzene	0.1265 0.0358	0.0394	0.0052	0.5559			
Cyclohexane	0.0338	0.0177 0.1455	0.0076 0.0371	0.0316 0.5707			
2-Methylhexane 2,3-Dimethylpentane	0.7363	0.1433	0.0371	0.5102			
3-Methylhexane	0.7303	0.2506	0.0661	0.8294			
•							
n-Heptane	0.9793	0.2182	0.0454	1.0401			
Methylcyclohexane	0.5567	0.1322	0.0343 0.0473	2.0397			
2,4-Dimethylhexane 2,3,4-Trimethylpentane	0.8914 2.8710	0.0382 0.0222	0.0473	0.1030 0.0523			
Toluene	0.5115	0.0222	0.1733	0.1805			
2,3-Dimethylhexane	0.1770	0.0270	0.0127	0.0840			
2-Methylheptane	0.2675	0.0826	0.0169	0.6672			
3-Ethylhexane	0.2710	0.0351	0.0097	0.3136			
n-Octane	1.7033	0.1645	0.0527	0.6727			
Ethylbenzene	1.5428	0.0704	0.0429	0.5052			
p-Xylene	0.7140	0.0002	0.0065	0.0000			
m-Xylene	0.6658	0.0293	0.0137	0.5832			
o-Xylene	0.4854	0.0184	0.0055	0.2485			
n-Nonane	0.1867	0.0000	0.0067	0.3525			
i-Propylbenzene	0.0700	0.0005	0.0000	0.0516			
n-Propylbenzene	0.4185	0.0134	0.0046	0.1527			
3-Ethyltoluene	0.3413	0.0154	0.0000	0.1630			
1,3,5-Trimethylbenzene	0.4177	0.0006	0.0000	0.1066			
2-Ethyltoluene	0.1949	0.0020	0.0000	0.0694			
t-butylbenzene 1,2,4-Trimethylbenzene	0.4297 0.3591	0.0000 0.0009	0.0000 0.0000	0.0000 0.2217			
i-butylbenzene	0.3391	0.0009	0.0000	0.0500			
s-butylbenzene	0.2913	0.0007	0.0000	0.0608			
•							
n-Decane	0.1863	0.0004	0.0000	0.0000			
1,2,3-Trimethylbenzene 1,3-Diethylbenzene	0.2014 0.3057	0.0208 0.0006	0.0000	0.1393 0.0486			
1,4-Diethylbenzene	0.3037	0.0000	0.0000	0.0457			
n-butylbenzene	0.4772	0.0000	0.0000	0.0000			
1,2-diethylbenzene	0.2090	0.0000	0.0000	0.0000			
n-undecane	0.6217	0.0000	0.0000	0.0000			
Other C4 Other C5	0.2737 0.0574	0.0000 0.3113	0.0000 0.0918	0.0000 0.9634			
Other C6	7.5924	3.7219	0.0918	5.6426			
Other C7	12.3951	2.5815	0.7104	5.4870			
Other C8	14.6463	1.0133	0.3623	5.4826			
Other C9	13.7861	0.2699	0.1006	2.7415			
Other C10	11.5726	0.0440	0.0157	0.6598			
Other C11	4.6614	0.0181	0.0000	0.1404			

Table 13 - West Coyote Summary Hydrocarbon Species by % Mass

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	OF-70	OF-71	OF-72	OF-73
Methane	58.1224	35.6628	15.1756	33.8652
Ethane	4.7094	3.3726	5.6015	5.6250
Propane	5.4105	5.2351	10.5062	8.0447
i-Butane	3.2893	3.6774	6.7594	3.6714
n-Butane	5.4490	8.0761	12.7356	7.9733
2,2-dimethylpropane	0.0451	0.0556	0.0896	0.0445
i-Pentane	3.3785	6.4922	8.4747	5.6750
n-Pentane	2.2557	4.1816	5.4918	4.0613
2,2-Dimethylbutane	0.0626	0.0233	0.1885	0.0000
Cyclopentane	0.2334	0.0000	0.0000	0.9262
,3-Dimethylbutane	0.0000	0.5183	0.6525	0.4254
2-Methylpentane	1.1015	0.6451	2.6275	2.3633
3-Methylpentane	0.7976	0.8300	1.9876	1.7445
n-Hexane	0.8718	1.9254	1.9240	1.9775
Methylcyclopentane	1.2895	3.4133	0.0000	3.2691
2,4-Dimethylpentane	0.0657	0.1657	0.1842	0.1464
Benzene	0.2862	1.0242	0.5061	0.7648
Cyclohexane	0.0141 0.2558	0.0455	0.0430 0.5803	0.0375 0.6403
2-Methylhexane 2,3-Dimethylpentane	0.2338	0.6520 0.4700	0.5803	0.0403
3-Methylhexane	0.2133	0.4765	0.3827	0.9254
•				
n-Heptane Methylcyclohexane	0.0516 0.8363	1.0903 0.0000	0.9119 0.0000	1.2199 1.9907
2,4-Dimethylhexane	0.0436	0.3761	0.0000	0.6066
2,3,4-Trimethylpentane	0.4135	0.6770	0.0503	0.0362
Toluene	0.0930	0.2632	0.2392	0.4144
2,3-Dimethylhexane	0.0351	0.0644	0.0690	0.0570
2-Methylheptane	0.3157	0.0911	0.4542	0.0000
3-Ethylhexane	0.1527	0.2564	0.2328	0.2375
n-Octane	0.1655	0.6430	0.2912	0.2312
Ethylbenzene	0.2061	0.2579	0.2439	0.2070
p-Xylene	0.2752	0.3141	0.2734	0.2357
m-Xylene	0.1314	0.0000	0.1329	0.0000
o-Xylene	0.1084	0.1187	0.1125	0.0911
n-Nonane	0.1806	0.0450	0.1687	0.0945
i-Propylbenzene	0.0104	0.0099	0.0093	0.0072
n-Propylbenzene	0.0494	0.0382	0.0499	0.0304
3-Ethyltoluene	0.0245	0.0187	0.0229	0.0145
1,3,5-Trimethylbenzene 2-Ethyltoluene	0.0422 0.0419	0.0000 0.0222	0.0435 0.0441	0.0000
t-butylbenzene	0.0419	0.0222	0.0441	0.0203
1,2,4-Trimethylbenzene 0.0150	0.0092	0.0137	0.0220	0.0150
i-butylbenzene	0.0000	0.0000	0.0000	0.0027
s-butylbenzene	0.0000	0.0115	0.0000	0.0082
n-Decane	0.0000	0.0000	0.0933	0.0255
1,2,3-Trimethylbenzene	0.0156	0.0101	0.0161	0.0075
1,3-Diethylbenzene	0.0084	0.0000	0.0000	0.0018
1,4-Diethylbenzene	0.0000	0.0131	0.0000	0.0090
n-butylbenzene	0.0146	0.0000	0.0150	0.0063
1,2-diethylbenzene	0.0046	0.0000	0.0000	0.0019
n-undecane	0.0000	0.0000	0.0000	0.0084
Other C4	0.0000	0.0000	0.0000	0.0000
Other C5	0.3807	4.2101	1.0699	0.1301
Other C6	2.3344	5.1428	9.4645	5.1712
Other C7	1.7070	5.1750	5.3237	3.2849
Other C9	2.4206	2.5361	2.8911	2.4562
Other C9 Other C10	1.2098 0.4144	1.0006	1.2675	0.6445
Other C11	0.4144	0.1483 0.0283	0.4558 0.0696	0.1150
Other CIT	0.05/1	0.0483	0.0090	0.0146

Table 14 - Database Format

yclohex	0000	0.1322	5	.1040	0.3697	.0255	0.0307	.0293	0000	0.0237	0.0177	.0486	.0164	6120	.0085	0109	.0075	.0177	0000	0000	0000	0000	0000	.0122	0000	0000	0.0059	000	.0052	0000	.0358	.0177	9/007	.0316	.0141	.0455	.0430	.0375
ں •	_	_	_	0.2571									_	_		_		_						_								_		_	0.2862 0	_	-	-
e B		0.2317 (_	0.0469 (
2,				0.0153																																		
9				0.3656	_		_	_						_	_					_			_		_												_	
	0.000	0.0737	0.0/12	0.0696	0.000	0.6783	0.7795	0.6824	1.6037	0.1099	0.0000	0.4636	1.4428	1.6061	0.6445	0.9477	0.7538	1.0913	1.4123	0.0000	0.0000	1.1323	0.6022	3.7394	0.0000	4.9084	0.0000	0.8659	1.0630	0.000	1.0717	0.6593	0.2066	1.9294	0.7976	0.8300	1.9876	1.7445
= .	0.000	0.0203	0.01 /4	0.000 0.000 0.000	0.0000	1.0121	1.1492	0.9909	1.7049	9066:0	1.0162	0.5465	1.2021	1.7627	1.0353	1.3757	1.1674	1.0834	2.1277	0.0223	0.0031	1.5351	0.6920	5.8657	4.0751	6.1335	0.0000	0.0071	0.000	0.0000	1.2635	0.8062	0.2607	2.6425	1.1015	0.6451	2.6275	2.3633
3.Dime 2	0.3033	1.3302	1007.1	0.8293	2.9941	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.3293	0.1474	0.0000	0.0000	0.0000	0.0000	0.0191	0.0011	0.0000	0.000	0.000	0.000	0.0000	1.5218	1.1875	0.0000	0.0000	0.3434	0.2522	0.1145	0.0000	0.0000	0.5183	0.6525	0.4254
Cyclopen 2	0.000	0.0000	0.0000	0.0000	0000	0.4262	0.4740	0.4656	0.2939	0.4103	0.1599	0.7297	0.2727	0.000	0.000	0.1801	0.1537	0.2917	0.6577	0.0000	0.0000	0.2525	0.1323	0.000	0.000	1.0410	0.0000	0.0000	0.0000	0.4227	0.4349	0.0000	0.0000	0.5612	0.2334	0.0000	0.0000	0.9262
2,2-Dime (0.3323	0.3794	0.040	00500	0.9194	0.1824	0.1976	0.1976	0.0925	0.1790	9960.0	0.3145	0.0877	0.0964	0.0438	0.0407	0.0409	0.0828	0.2502	0.000	0.0050	0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0520	0.000	0.0235	0.0338	0.060	0.0351	0.1539	0.0626	0.0233	0.1885	0.0000
n-Pentan	0.000	0.0321	0.020	0.0054	96900	2.7182	1.4220	3.3991	3.2146	3.4792	1.5078	3.5079	3.0220	8.3204	3.3931	3.9112	3.8510	5.6848	4.3558	0.0456	0.0079	0.8501	1.6241	18.2855	4.3522	5.2835	5.1406	4.6708	5.8342	2.6707	2.2614	1.9546	0.7548	5.4645	2.2557	4.1816	5.4918	4.0613
i-Pentane	0.000	0.1803	0.1330	0.1349	0.4758	2.8767	1.5246	3.3797	2.0964	3.6524	1.6843	1.8193	4.4784	5.9460	2.9425	3.5109	3.7319	5.0878	5.3812	0.0535	0.0080	2.8269	1.6489	18.5162	3.5461	4.3902	5.8607	5.7925	6.7579	2.5646	2.2168	2.5187	1.1618	8.6462	3.3785	6.4922	8.4747	5.6750
2,2-dimet	0.000	0.3083	0157.0	0.03/0	0.3897	0.1106	0.1170	0.1195	0.0427	0.1169	0.6509	0.1633	0.0420	0.0456	0.0203	0.0185	0.0251	0.0415	0.2065	0.0794	0.0554	0.0114	0.000	0.0443	0.000	0.0000	0.0146	0.0162	0.0190	0.000	0.0220	0.0256	0.0258	0.1059	0.0451	0.0556	0.0896	0.0445
n-Butane	0.1623	0.0842	6.000	0.0914	0.2139	10.3318	6.7414	10.8072	17.3072	11.4358	3.3683	15.2084	13.2046	17.5464	7.7710	8.2760	9.7694	14.0011	9/19/9	0.1228	0.0335	8.2204	4.444	16.7562	2.4984	0.0000	14.4739	16.1895	19.0352	2.1218	2.1302	3.9861	1.9669	14.2861	5.4490	8.0761	12.7356	7.9733
i-Butane	0.0000	0.0647	0.0001	0.1001	0.3003	3.1748	3.3993	3.4171	5.7194	3.8778	4.2802	3.2037	5.0340	1.9291	2.7121	2.5031	3.0755	4.2843	2.1106	0.0375	0.0213	3.1034	1.5022	4.5482	0.000	1.0505	6.0712	7.6461	7.9999	0.6395	0.8152	2.2601	1.6328	7.6645	3.2893	3.6774	6.7594	3.6714
Propane	0.1499	0.0955	0.000	0.0716	0.3025	13.0885	14.8836	17.2663	17.0718	17.7471	15.3786	12.6201	14.1825	20.3860	13.5873	10.3987	13.3879	16.7611	4.5376	0.1836	0.1861	14.1404	11.3004	4.9484	1.3702	0.0000	18.9621	23.1831	25.1314	4.9068	0.8504	3.9190	1.9722	3.7709	5.4105	5.2351	10.5062	8.0447
Ethane	0.0751	0.1565	1 7017	0.2717	0.4191	7.9019	7.6800	12.7117	9.5479	15.4250	8.4997	3.7104	7.5402	13.8534	10.1622	6.8113	9.2589	7.9440	5.4703	0.5781	0.6958	8.8839	20.1940	1.5655	1.6118	0.000	6.4585	/.5008	6.8363	9.0459	0.2429	3.4827	2.5933	8.6278	4.7094	3.3726	5.6015	5.6250
Methane	0.1010	81.3998	00110	95 9789	4.4862	44.8895	37.7408	33.4312	11.8005	31.9680	19.4226	35.1586	26.7810	0.6309	47.8262	44.8636	45.7334	25.6069	2.7544	95.9626	98.1996	40.6929	10.0741	8.0981	0.0000	0.000	26.3353	24.7704	12.8696	69.8572	0.0000	69.7258	86.2213	9.3724	58.1224	35.6628	15.1756	33.8652
		7 6	2 :	t Y	8	10	=	12	13	-14	-15	-16	:17	20	-21	-22	:-23	-24	-25	-58	:-27	9	7	45	-43	4	OF-50	₹ ?	-52	- . 53	9	-61	-62	-63	-70	-71	-72	-73

I. Discussion of Results

To assess variability introduced by the sampling process, duplicate samples OF-2 and OF-3 were taken from the same point, within 30 minutes of each other. Table 15 shows that these samples agree fairly well with each other. The largest difference was in the methane values: 81.4 vs. 62.0 %. These samples were collected by bagging a valve, and capturing the bagged emissions into a stainless steel canister. It was impossible to keep the sampling time constant for these two runs. The "leak rate" of the sampled valve was not constant. Another potential source of variability is a compositional change in the emissions with respect to time. In any case, most constituents other than methane agreed within 0.1 % absolute, or 30 % relative. These values probably represent realistic estimates of the overall uncertainty in the values listed in the summary tables.

Three samples (OF-43,44 and 60) were found to contain no methane. These samples were obtained from open sumps. The methane content of samples taken directly from well heads at the Kern River Facility ranged from 5 to 80 % of the total hydrocarbons. Since methane was determined separately from the other hydrocarbons, a sensitivity study was undertaken, to estimate the effect of errors in the methane concentration on the overall results. The results of this study (Table 16) show that errors in the methane analysis should not unduly influence the overall results. In general, the overall uncertainty in the % composition values is proportional to the error in the methane concentration.

The analytical methods used in this study yielded chromatograms containing as many as several hundred peaks. As discussed earlier, some peaks remained unidentified, and were listed as "Other Cn". Table 17 shows information on these compounds. The study-wide average for "Others" was 17%. In other words, an average of 83 % of the total hydrocarbon mass was identified. There are a few notable deviations from this average. The average value for "others" in the Kern River field was 36 %, more than twice the overall average. Samples OF-1 and OF-6 show values of about 75 % unidentified compounds. This field produces heavy crude (API gravity: 13.60) by steamflood. Sample OF-1 came from the headspace of a gage tank open to the atmosphere (no vapor recovery), in close proximity to well 406. The oil in the tank was at 720 C. These two conditions evidently resulted in a depletion of the lighter hydrocarbons, which contribute a fair fraction of the mass for samples taken at other fields. Unlike most other samples, OF-1 showed most of its hydrocarbon mass above the C7 range, with a number of "heavy" peaks not found in other samples. Well head samples taken at well 406 (OF-2 and OF-3) contained 60 - 80 % methane. It is likely that the elevated temperature of all samples in this field is responsible for the higher amounts of heavy hydrocarbons not identified.

Consistent with the original Request for Proposal, results from all light, medium and heavy samples have been summarized in Table 18.

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Table 15 - Sampling Variability

Table 13 - Sampling V	ariability			
	OF-02	OF-03	DIFFERENCE	
	OF-02	Or-03	absolute	% relative to mean
Methane	81.3998	62.0949	19.30	26.91
Ethane	0.1565		0.04	25.23
Propane	0.0955		0.02	20.07
i-Butane	0.0647		0.01	19.61
n-Butane	0.0842		0.02	20.80
2,2-dimethylpropane	0.3083		0.06	20.50
i-Pentane	0.1803		0.02	14.61
n-Pentane	0.0321		0.01	24.88
2,2-Dimethylbutane	0.3794		0.03	8.44
Cyclopentane	0.0000		0.00	N/A
2,3-Dimethylbutane	1.3302		0.04	3.21
2-Methylpentane	0.0203		0.00	15.31
3-Methylpentane	0.0737		0.00	3.41
n-Hexane	0.0194		0.01	81.78
Methylcyclopentane	0.0121		-0.13	-168.42
2,4-Dimethylpentane	0.2317	0.2654	-0.03	-13.54
Benzene	0.0137	0.0000	0.01	N/A
Cyclohexane	0.1322	0.1564	-0.02	-16.75
2-Methylhexane	0.6399	0.7923	-0.15	-21.28
2,3-Dimethylpentane	0.0000	0.0000	0.00	N/A
3-Methylhexane	0.0223	0.0228	-0.00	-2.15
n-Heptane	0.0000	9.0000	0.00	N/A
Methylcyclohexane	0.0158	0.0169	-0.00	-6.24
2,4-Dimethylhexane	0.1780	0.2580	-0.08	-36.68
2,3,4-Trimethylpentane	0.1985	0.2951	-0.10	-39.10
Toluene	0.0800	0.1192	-0.04	-39.29
2,3-Dimethylhexane	0.0466	0.0566	-0.01	-19.50
2-Methylheptane	0.0298	0.0513	-0.02	-52.97
3-Ethylhexane	0.1108	0.1775	-0.07	-46.26
n-Octane	0.8900	1.4281	-0.54	-46.42
Ethylbenzene	0.4798	0.7963	-0.32	-49.61
p-Xylene	0.0155	0.0250	-0.01	-46.99
m-Xylene	0.0091	0.0096	-0.00	-4.97
o-Xylene	0.1397	0.2040	-0.06	-37.39
n-Nonane	0.0804	0.1463	-0.07	-58.18
i-Propylbenzene	0.0751	0.1261	-0.05	-50.64
n-Propylbenzene	0.0704	0.1432	-0.07	-68.25
3-Ethyltoluene	0.0754	0.0701	0.01	7.34
1,3,5-Trimethylbenzene	0.1059	0.2325	-0.13	-74.84
2-Ethyltoluene	0.1053	0.2072	-0.10	-65.23
t-butylbenzene	0.1515	0.2642	-0.11	-54.27
1,2,4-Trimethylbenzene	0.1777	0.3203	-0.14	-57.27
i-butyibenzene	0.0000	0.0000	0.00	N/A
s-butylbenzene	0.1154	0.2455	-0.13	-72.06
n-Decane	0.0767	0.1528	-0.08	-66.30
1,2,3-Trimethylbenzene	0.1167	0.2233	-0.11	-62.71
1,3-Diethylbenzene	0.0883	0.2133	-0.12	-82.85
1,4-Diethylbenzene	0.0874	0.2261	-0.14	-88.47
n-butylbenzene	0.0273	0.1696	-0.14	-144.46
1,2-diethylbenzene n-undecane	0.0729	0.1544	-0.08	-71.68
Other C4	0.0000	0.1151	-0.12	N/A
Other C5	0.0000	0.0000	0.00	N/A
Other C6	0.0000 0.6617	0.0000	0.00	N/A
Other C7		0.7074	-0.05	-6.67
Other C8	2.7837 3.1244	4.5832 5.1630	-1.80 2.04	-48.85 49.31
Other C9	2.7101	5.1639 5.6391	-2.04 2.03	-49.21 70.16
Other C10	1.8284		-2.93 4.26	-70.16
Other C11	0.0751	6.0923 5.4074	-4.26 5.22	-107.67
Other CII	0.0731	3.4074	-5.33	-194.52
AVERAGE1 : all values		AVERAGE1	-0.00	-31.35
	e OTHER		-0.06	-27.99
AVERAGE2: excluding methane	« UTHEKS	AVERAGE2	-0.00	- 41.33

Table 16 - Methane Sensitivity Analysis Results

	Meth	Methane area, % relative to Nominal Value													
	100	90	110	125	75	150	50								
C1	87.038	85.803	88.076	89.355	83.433	90.969	77.051								
C2	2.194	2.403	2.018	1.802	2.804	1.529	3.885								
C3	1.507	1.651	1.387	1.238	1.926	1.050	2.668								
C4	5.126	5.614	4.715	4.210	6.551	3.571	9.075								
C5	0.970	1.063	0.893	0.797	1.240	0.676	1.718								
C6	1.901	2.082	1.749	1.561	2.429	1.324	3.365								
C7	0.939	1.028	0.864	0.771	1.200	0.654	1.662								
C8	0.292	0.320	0.268	0.240	0.373	0.203	0.517								
C9	0.033	0.036	0.031	0.027	0.042	0.023	0.059								
C10	0.000	0.000	0.000	0.000	0.000	0.000	0.000								
C11	0.000	0.000	0.000	0.000	0.000	0.000	0.000								
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00								

ERRORS			n			
C1	-1.4%	1.2%	2.7%	-4.1%	4.5%	-11.5%
C2	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C3	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C4	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C5	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C6	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C7	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C8	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C9	9.5%	-8.0%	-17.9%	27.8%	-30.3%	77.1%
C10	N/A	N/A	N/A	N/A	N/A	N/A
C11	N/A	N/A	N/A	N/A	N/A	N/A
TOTAL	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

Table 17 - OIL FIELD SUMMARY - "OTHER Cn", by % Mass

	0.1 04	0.1 05	0.1 00	0.1 0.5					
OE 01	Other C4	Other C5	Other C6	Other C7	Other C8	Other C9	Other C10	Other C11	TOTAL
OF-01 OF-02	0.0000	0.0000	0.0000	2.7537	9.6620	24.3261	30.0711	10.0782	76.89
	0.0000	0.0000	0.6617	2.7837	3.1244	2.7101	1.8284	0.0751	11.18
OF-03	0.0000	0.0000	0.7074	4.5832	5.1639	5.6391	6.0923	5.4074	27.59
OF-04	0.1460	0.0566	0.6329	2.6022	5.9405	10.3142	6.6704	0.3234	26.69
OF-05	0.0000	0.0000	0.0000	0.4848	0.7901	0.8362	0.3693	0.0275	2.51
OF-06	0.0000	0.0000	3.0064	21.5246	22.4750	19.7780	6.7337	0.0353	73.55
	iver Average		2 2152	1 2005	0.7010	2.510.4			36.40
OF-10	0.5783	1.4612	2.2153	1.3296	0.7813	0.3196	0.1121	0.0219	6.82
OF-11	6.1069	3.0812	3.3493	2.3796	1.3165	0.6090	0.1073	0.0068	16.96
OF-12	0.0000	0.7107	3.1000	1.5896	1.0459	0.4462	0.0851	0.0040	6.98
OF-13	5.2441	6.5695	3.6424	2.0599	0.6321	0.1228	0.0000	0.0000	18.27
OF-14	0.0577	1.3404	1.9094	1.3557	0.6379	0.2824	0.0975	0.0098	5.69
OF-15	13.7463	9.1198	6.4305	4.3198	0.9180	0.3332	0.0000	0.0000	34.87
OF-16	0.0000	1.2993	6.2250	3.7814	1.9979	0.6220	0.0177	0.0000	13.94
OF-17	2.5913	6.2761	3.0361	1.2699	0.4258	0.0753	0.0000	0.0000	13.67
	s Average								14.65
OF-20	0.0000	2.8126	6.9258	3.0713	1.8956	0.7019	0.1335	0.0394	15.58
OF-21	0.0000	0.0000	0.5288	3.6994	1.4513	0.9881	0.0484	0.0092	6.73
OF-22	0.0000	0.6376	5.9315	2.9653	1.6682	0.6194	0.0776	0.0018	11.90
OF-23	0.0000	0.5484	3.7219	1.0916	0.4752	0.0943	0.0302	0.0056	5.97
OF-24	0.0000	1.6789	4.2202	3.0840	0.9441	0.1285	0.0331	0.0000	10.09
OF-25	0.0000	1.3806	8.7054	15.5060	11.9369	6.6643	1.3815	0.3470	45.92
OF-26	0.0000	0.0553	0.0935	0.1773	0.6540	0.8882	0.5560	0.1279	2.55
OF-27	0.0000	0.0126	0.0171	0.0106	0.0655	0.2110	0.2885	0.0000	0.61
	Average								12.42
OF-40	1.1117	3.3706	1.6494	1.3692	1.3995	0.6859	0.3521	0.0684	10.01
OF-41	0.0000	0.6062	2.0726	2.4995	5.4748	8.4377	5.1144	1.7402	25.95
OF-42	0.0000	2.7335	2.6472	0.8324	0.0995	0.0106	0.0000	0.0000	6.32
OF-43	0.0000	0.0000	0.0000	0.0000	5.4339	8.1739	0.0000	0.0000	13.61
OF-44	0.0000	1.3944	9.5263	5.7191	4.5759	1.7149	1.5896	0.0000	24.52
Cat Can	yon Average								16.08
OF-50	0.0000	2.0335	2.4888	1.7315	0.9871	0.4512	0.0890	0.0056	7.79
OF-51	0.0246	1.4400	1.2186	0.5669	0.3069	0.2100	0.0568	0.0000	3.82
OF-52	0.0060	2.4045	3.7835	1.0877	0.5952	0.2615	0.0577	0.0123	8.21
OF-53	0.0000	1.3762	0.9365	0.6074	0.5527	0.8476	0.3196	0.0092	4.65
Ventura	Average			····					6.12
OF-60	0.2737	0.0574	7.5924	12.3951	14.6463	13.7861	11.5726	4.6614	64.98
OF-61	0.0000	0.3113	3.7219	2.5815	1.0133	0.2699	0.0440	0.0181	7.96
OF-62	0.0000	0.0918	0.7104	0.5625	0.3413	0.1006	0.0157	0.0000	1.82
OF-63	0.0000	0.9634	5.6426	5.4870	5.4826	2.7415	0.6598	0.1404	21.12
	ton Average				2.,020		0.0020	5.1707	23.97
OF-70	0.0000	0.3807	2.3344	1.7070	2.4206	1.2098	0.4144	0.0571	8.52
OF-71	0.0000	4.2101	5.1428	5.1750	2.5361	1.0006	0.1483	0.0283	18.24
OF-72	0.0000	1.0699	9.4645	5.3237	2.8911	1.2675	0.4558	0.0696	20.54
OF-73	0.0000	0.1301	5.1712	3.2849	2.4562	0.6445	0.1150	0.0146	11.82
	yote Average			2.2019	2.7502	0.0443	0.1150	0.0170	14.78
	2								1-7.70
ALL FIE	ELD AVERA	AGE							17.77
					-				

Table 18 - OIL FIELD SUMMARY BY TYPE OF CRUDE

	HEAVY		MEDIUM	_	LIGHT	
	AVERAGE	σ	AVERAGE	σ	AVERAGE	σ
Methane	40.3306	39.9900	35.6790	14.7932	22.3296	18.2560
Ethane	3.1335 2.6816	5.0954 4.0563	7.0480	2.2906	11.4976	2.9810
Propane i-Butane	1.4099	2.0243	13.3730 4.2404	6.0151 1.9756	16.8342 3.7037	2.5576 1.4627
n-Butane	3.4299	5.0578	10.8996	4.4188	11.4858	6.1301
2,2-dimethylpropane	0.1282	0.1730	0.0576	0.0477	0.1753	0.2683
i-Pentane	2.8847	4.5520	4.4628	1.9424	3.2643	1.6812
n-Pentane	2.5220	4.3954	3.8639	1.2808	3.9830	2.5560
2,2-Dimethylbutane	0.1694	0.2482	0.0934	0.0938	0.1017	0.0487
Cyclopentane	0.1806	0.3014	0.2860	0.2773	0.1728	0.1809
2,3-Dimethylbutane	0.4154	0.7770	0.2691	0.4791	0.0953	0.1455
2-Methylpentane	1.4184	2.0159	0.9545	0.7764	1.3019	0.3951
3-Methylpentane	0.8937	1.3878	0.8830	0.5298	0.7929	0.7804
n-Hexane	1.4916	2.1232	1.4227	0.4918	2.1744	1.0517
Methylcyclopentane	1.4230	1.9021	1.7263	1.1250	1.8375	1.3330
2,4-Dimethylpentane	0.1154	0.1537	0.0873	0.0603	0.0865	0.0252
Benzene	1.3177	3.1774	0.2629	0.2799	0.2950	0.1856
Cyclohexane	0.0482	0.0941	0.0211	0.0164	0.0144	0.0100
2-Methylhexane	0.3843	0.4086	0.3014	0.1874	0.3788	0.1829
2,3-Dimethylpentane	0.3743	0.5728	0.2565	0.1468	0.2214	0.0672
3-Methylhexane	0.4196	0.6670	0.4470	0.2466	0.2200	0.2543
n-Heptane	0.8177	1.3746	0.5367	0.3417	0.7939	0.4691
Methylcyclohexane	0.8028	1.4618	0.7113	0.6985	0.7265	0.6228
2,4-Dimethylhexane	0.2177	0.3263	0.1070	0.1634	0.0356	0.0542
2,3,4-Trimethylpentane	0.2920	0.6669	0.2278	0.2963	0.0668	0.1047
Toluene	1.2527	2.8219	0.1943	0.1002	0.3306	0.2602
2,3-Dimethylhexane 2-Methylheptane	0.0579 0.1747	0.0676 0.2636	0.0300 0.1206	0.0217 0.1250	0.0233 0.0943	0.0166 0.1876
3-Ethylhexane	0.2368	0.2842	0.1200	0.1230	0.0794	0.1878
5-Diffyiteadire	0.2500	V.2042	0.0723	0.0070	0.0754	0.0717
n-Octane	1.0096	1.0595	0.2069	0.1473	0.2415	0.1326
Ethylbenzene	0.8447	1.1022	0.1289	0.0737	0.0939	0.0534
p-Xylene	0.4054	1.1508	0.1054	0.1068	0.0216	0.0210
m-Xylene	0.2678	0.4639	0.0546	0.0429	0.1127	0.0849
o-Xylene	0.5411	1.0675	0.0541	0.0344	0.0400	0.0329
n-Nonane	0.5212	1.0144	0.0601	0.0515	0.0652	0.0504
i-Propylbenzene	0.0739	0.1086	0.0041	0.0040	0.0029	0.0031
n-Propylbenzene	0.1692	0.2054	0.0197	0.0161	0.0176	0.0128
3-Ethyltoluene	0.1576	0.1963	0.0097	0.0088	0.0051	0.0055
1,3,5-Trimethylbenzene	0.1714	0.3033	0.0089	0.0150	0.0083	0.0111
2-Ethyltoluene	0.1710	0.2772	0.0121	0.0142	0.0070	0.0108
t-butylbenzene	0.2062	0.3513	0.0079	0.0083	0.0045	0.0066
1,2,4-Trimethylbenzene	0.5156	1.1864	0.0105	0.0118	0.0099	0.0161
i-butylbenzene s-butylbenzene	0.0888 0.1747	0.1961 0.3680	0.0016 0.0032	0.0036 0.0053	0.0012 0.0024	0.0026
3-outytoenzene	0.1747	0.5000	0.0032	0.0055	0.0024	0.0034
n-Decane	0.1078	0.2289	0.0161	0.0244	0.0061	0.0078
1,2,3-Trimethylbenzene	0.1848	0.3104	0.0090	0.0146	0.0011	0.0024
1,3-Diethylbenzene	0.1971	0.3609	0.0027	0.0067	0.0026	0.0057
1,4-Diethylbenzene	0.1658	0.3163	0.0022	0.0043	0.0008	0.0019
n-butylbenzene	0.1157	0.2629	0.0027	0.0051	0.0027	0.0038
1,2-diethylbenzene	0.1157	0.2365	0.0004	0.0012	0.0076	0.0170
n-undecane	0.1158	0.3117	0.0028	0.0057	0.0018	0.0041
Other C4	0.0851	0.2659	0.5817	1.6110	3.8096	5.9979
Other C5	0.6130	1.0097	1.7962	1.5924	3.9684	3.7846
Other C6	2.6326	3.1626	3.8962	2.1408	3.8874	2.7817
Other C7	4.5485	5.9753	2.3109	1.4970	2.9012	1.2015
Other C8	5.4600	5.9669	1.3375	0.8678	1.1070	0.5526
Other C9	5.9605	7.1701	0.5505	0.3784	0.4857	0.3519
Other C10	4.0744	7.2816	0.1325	0.1391	0.0559	0.0593
Other C11	1.2806	2.7259	0.0148	0.0207	0.0117	0.0162

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- 1 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711
- 2. Procedures for the Sampling and Analysis of Atmospheric Toxic Compounds, California Air Resources Board, Haagen-Smit Laboratory Division

APPENDIX A - Key Personnel Contacts

Name	Company	Telephone
Ron James, Div. Supt.	Union Oil	(805) 543-3108
Steven Woodruff	Chevron	(805) 395-6312
Steven Zeeman	Chevron	(415) 842-0025
Michael Rutledge	Texaco	(805) 762-7331
Fred Hagist, Env. Spec.	Kern River	(805) 399-2961
Mark Shimarian	THUMS Long Beach Co.	(213) 436-9211
Jack Caufield	Bechtel	(805) 763-6632
Darryl Gunderson	Shell	(805) 326-5279
Sam Duran	Texaco	(805) 648-8243

APPENDIX B - PHOTOGRAPHS OF SELECTED SAMPLING SITES

Key for Oil Field Photos

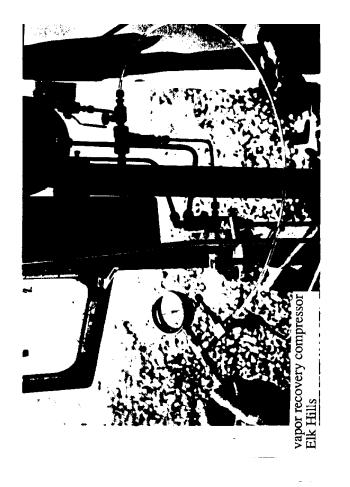
- 1. bagged valve sampling Kern River
- 2. tank roof hatch sampling Kern River
- 3. Teflon bag buffer Belridge
- 4. casing valve sampling Belridge
- 5. production header Belridge
- 6. vapor recovery compressor Elk Hills
- 7. sump sampler Cat Canyon
- 8. sump sampler Cat Canyon
- 9. sump cover Wilmington
- 10. sump sampling Wilmington
- 11. flux box on sump Wilmington
- 12. casing valve Wilmington

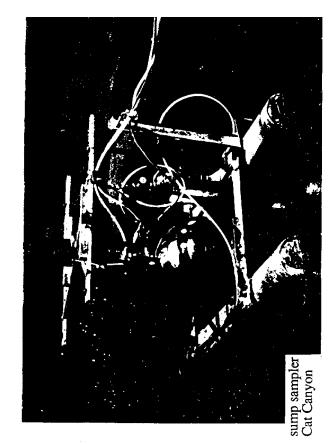


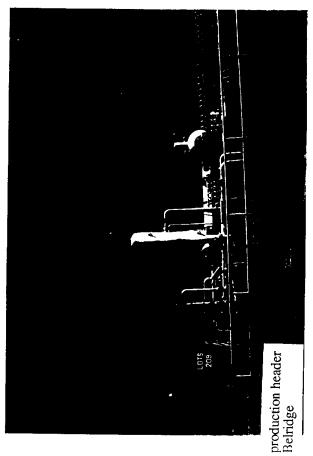








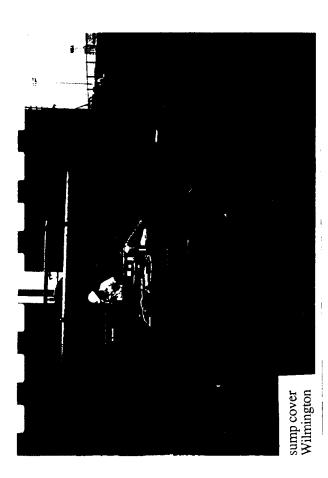


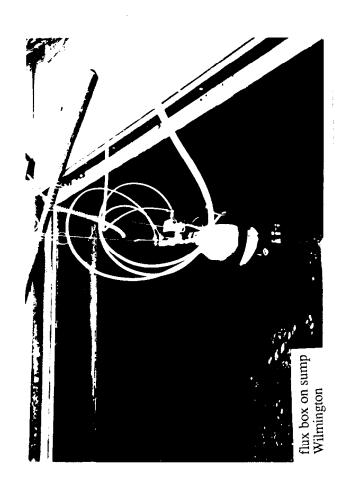












APPENDIX C -Protocol for Sampling Fugitive Emissions from Oil Production Facilities

1. Applicability

- 1.1 The procedures described herein will be applied to sampling fugitive hydrocarbon emissions from a variety of sources found in California oil production fields.
- 1.2 Sources to be tested by this procedure will have been screened for positive leakage by a soap bubble test (if applicable), and screened for positive hydrocarbon content by a portable hydrocarbon analyzer (OVA 128 or Gastech Analyzer).

2. Method

- 2.1 Leaking components will be isolated by a Teflon shroud.
- 2.2 Emissions will be collected in evacuated, passivated stainless steel canisters.
 - 2.2.1 If component leak rate is high, emissions filling the shroud will be collected directly.
 - 2.2.2 If component leak rate is low, zero air will be permitted to flow into the shroud, and diluted emissions at the shroud outlet will be collected as above.
- 2.3 Sumps and pits will have a portion of their surface isolated by a flux chamber.
- 2.4 Zero air will be permitted to enter the chamber and mix with the emissions.
- 2.5 The diluted emissions at the chamber outlet will be collected in evacuated stainless steel canisters.
- 2.6 The headspace of storage tanks will be accessed via roof hatches.
- 2.7 Tank headspace will be collected in evacuated stainless steel canisters.
- 2.8 Analysis will be performed, using gas chromatography, with flame ionization or mass spectrometric detection, as appropriate.

3. Components

- 3.1 A cylinder of zero air, containing less than 0.1 PPM hydrocarbons.
 - 3.1.1 A size 3 cylinder (6" x 10", 30 ft³ @ 2000 PSIG) of Ultra Zero Air, from Matheson, Cucamonga, CA.
 - 3.1.2 A non-contaminating manual central valve, #4351, CGA 590 from Matheson, Cucamonga, CA.
- 3.2 Teflon bags, various sizes from 3 liter to 20 liters, from Berghof, Inc., Concord, CA.
- 3.3 A rotameter to monitor flow of zero air, from Ace Glass, Vineland, NJ.
- 3.4 Adhesive tapes in a variety of widths.
- 3.5 SUMMA-passivated stainless steel canisters, 3.2 liter.
- 3.6 Stainless steel or other inert flux chamber.
- 3.7 Combination pressure-vacuum gauge for field check of canister pressure.
- 3.8 Teflon tubing, for use in sampling lines, Berghof, Concord, CA.

4. Procedure

- 4.1 The leaking component is isolated, a Teflon bag of appropriate size, sealed with tape or an elastic band.
 - 4.1.1 The shroud is leak-checked by inflation with zero air. Leaking seams are identified and repaired.
 - 4.1.2 The contents of the shroud are expelled by compression of the Teflon bag.
 - 4.1.3 If the component leak rate is high, the shroud will re-inflate.

- 4.1.4 Perform another empty/fill cycle.
- 4.1.5 Complete sample ID sheet with component description, and canister number.
- 4.1.6 Attach vacuum gauge to sampling canister, open canister valve just long enough to note and record pressure.
- 4.1.7 Attach sampling canister to shroud exit part.
- 4.1.8 When shroud is fully inflated, slowly open canister valve, and allow sample to fill canister.
- 4.1.9 When canister contents are at atmospheric pressure, close canister valve and remove canister from shroud.
- 4.1.10 If component leak rate is low, fill shroud by metering in zero air at no more than 500 mL/min. Allow at least 3 shroud volumes of air to flow before sampling as above.
- 4.2 For sumps and pits, place emission isolation chamber on surface.
 - 4.2.1 Meter in zero air at 2-5 liters/min. Allow at least 3 chamber volumes of air to flow before sampling.
 - 4.2.2 Perform canister pressure check as in 4.1.6.
 - 4.2.3 Attach canister to chamber outlet port, and slowly open canister valve.
 - 4.2.4 When canister contents are at atmospheric pressure, close canister valve and remove canister.
- 4.3 For storage tanks, locate access hatch.
 - 4.3.1 Perform canister pressure check as in 4.1.6.

- 4.3.2 Attach 1/4" O.D. stainless steel sampling probe to canister.
- 4.3.3 Open access hatch enough to insert probe well into tank headspace.
- 4.3.4 Open canister valve, and allow sample to fill canister.
- 4.3.5 When canister contents are at atmospheric pressure, close canister valve, withdraw sampling probe and close hatch.

APPENDIX D - ANALYTICAL METHODOLOGY AND CALIBRATION

5. ANALYTICAL METHODOLOGY AND CALIBRATION

5.1 Introduction to Analytical Methodology

Environmental Analytical Service, Inc. (EAS) performed the chemical analysis of diluted engine exhaust and bagged component samples using dedicated gas chromatographs (GC) equipped with flame ionization detectors (FID). The FID provides maximum sensitivity for hydrocarbons and has a selective response to hydrocarbon atoms. With proper gas chromatographic separation methods, the concentration of components in complex mixtures can be accurately determined. A GC equipped with a mass spectrometer detector (MSD) was used for confirmation of compound identities in collected samples. These methods provided complete compound speciation for all photochemically reactive organic compounds (PROC) as described in the EPA document <u>Guidance for the Collection and use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies</u> (Singh, 1980). The following sections describe the analytical methods EAS used for the fugitive emissions study.

5.1.1 Analysis of Methane

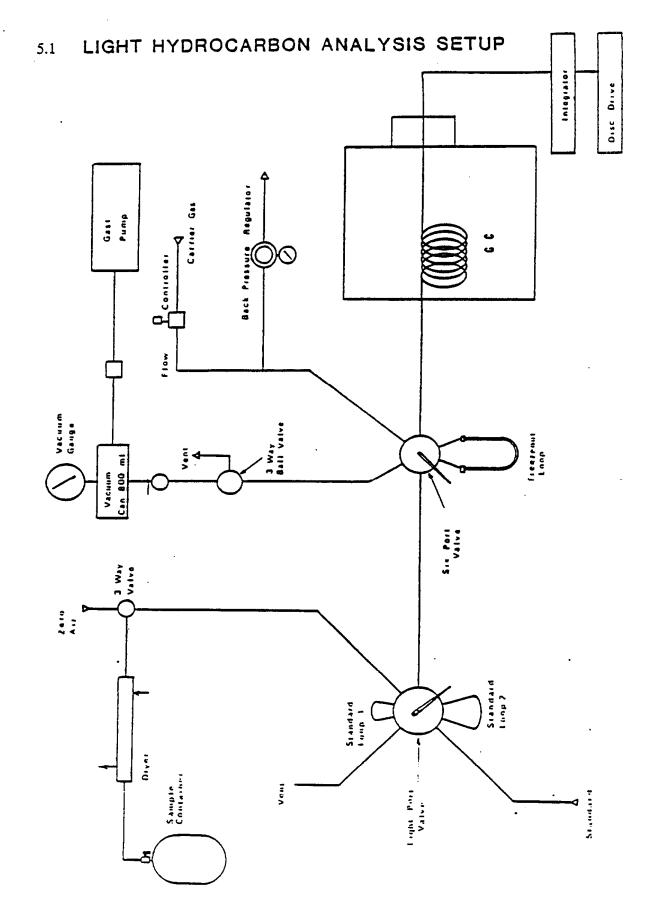
Methane in the collected samples was analyzed using a Carle AGC 100 isothermal gas chromatograph. The methane was separated from air and CO using a 6' Molecular Sieve 5A Column at 50 °C. The helium carrier gas flow rate used was 30 mL/min. Air pressure was maintained at 16 psig and hydrogen pressure at 22 psig, as recommended by the manufacturer. A 2.0 mL sampling loop was used to measure the sample size. The sample loop was kept in a thermostated oven to maintain constant volume. The peaks were integrated using a HP 3393A computing integrator which directly calculated the methane concentration in ppmC. The relative precision for methane at 1,725 ppbvC is 0.2 to 0.4%. The response has been demonstrated to be linear to 20 ppmvC.

5.1.2 Light Hydrocarbon Analysis (C2 to C4) at Low Concentrations

The light hydrocarbons were analyzed using a GC/FID packed column procedure. The column and procedure used for analysis is recommended by EPA and described in California Air Resources Board Method 104. The column used was 1/8" by 10' stainless steel packed with phenyl-isocyanate on Durapack 80/100 mesh. The gas chromatograph used was an HP 5890 with a Model HP3393A computing integrator equipped with chart readout. A 100 to 500 mL gas sample was concentrated using a glass bead freezeout loop procedure. The column was operated isothermally at 28 °C.

A diagram for the instrumental set-up for light hydrocarbon analysis is shown in Figure 5.1.1. The sample canister is connected to a counterflow dryer made of Nafion tubing. The dryer removes water vapor from the sample before analysis. The sample loop is immersed in a Dewar flask filled with liquid oxygen, which traps out hydrocarbons from C2 to C10 quantitatively. The sample is pulled through the glass bead freezeout loop by vacuum. The volume of sample was determined by measuring the pressure drop in a 1.2 liter canister. A precision vacuum test gauge was used to measure the pressure change from which the volume of sample can be calculated (see Section 6.3.3). The system can be used to accurately measure a sample size of 100 to 500 mL.

Once the constituents are trapped, the six port valve is switched from <load> to <analyze>, and the freezeout loop is placed in 80 °C water to thermally desorb the hydrocarbons. The desorbed compounds flow to a 1/8" by 10' stainless steel column packed with phenylisocyanate on Durapack 80/100 mesh. Analysis is performed isothermally at 28 °C. The column flow is controlled by column head pressure and is maintained at 20 psig to give a flow of 40 mL/min. The hydrocarbons are analyzed on a FID detector. The operating conditions are summarized in Table 5.1.



OPERATING CONDITIONS

```
METHANE -
    Flows -
                     30 ml/min
          Helium
          Hydrogen 30 ml/min
    Gas Pressures -
          Helium (Column Pressure) 40 psig
          Hydrogen (Flame) 24 psig
          Air (Flame) 15 psig
    Temperature Program - 50°C
    Detector Temperature - 150 C
    Sample Size - 1.0 ml
LIGHT HYDROCARBONS -
   Plows -
         Helium 29 ml/min
         Hydrogen 31 ml/min
               340 ml/min
         Air
   Gas Pressures -
         Helium (Column Pressure) 40 psig
         Hydrogen (Flame) 17.5 psig
         Air (Flame) 34 psig
   Temperature Program - 30 C
   Detector Temperature - 250 C
   Sample Size - 500 ml
HEAVY HYDROCARBONS -
   Flows -
              420 ml/min
         Air
          Nitrogen 43 ml/min
   Gas Pressures -
          Hydrogen (Column Pressure) 7 psig
                                      17 psig
          Hydrogen (Flame)
                                      35 psig
          Air (Flame)
          Nitrogen (Make-up Gas)
                                     30 psig
   Temperature Program - 20C for 2 min, Program Rate 6 C/min Detector Temperature - 275 C
    Sample Size - 500 ml
```

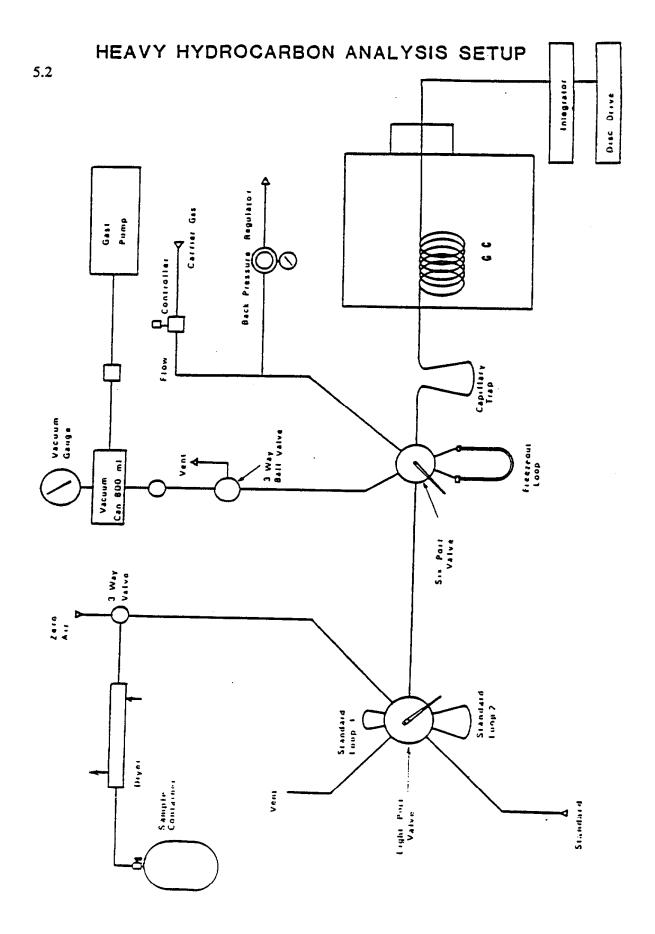
The peak areas were integrated using an HP 3393A computing integrator with chart recorder. The charts were examined to verify proper system operation and chromatographic resolution. The integrated data were used to calculate the concentration of the constituents. These results were compared with standard runs, and quantified against a commercial propane standard that is traceable to NBS standards (see Section 5.4.2). Response factors of hydrocarbons other than propane are based on carbon number and checked experimentally and against literature values (Dietz, 1967). Hard copies of the chromatograms, and integrated data are EAS proprietary materials which are stored permanently at the laboratory for a five year period. These materials are available for inspection by the client at the EAS laboratory and are not released in copy form to the client.

Analysis of Light Hydrocarbons (C2 to C6) at High Concentrations.

Some light hydrocarbons from bagged component samples were present at high concentrations. These samples were analyzed on the Carle AGC 100 GC using a 1/8" x 30' column containing 23 % SP-1700 on 80/100 Chromosorb PAW operating at 75 °C, isothermal. A 1.0 mL sample loop with backflush was used for direct injection. Concentrations in the 0.1 percent to 100 percent range were measured using a thermal conductivity detector (TCD). The precision for this method at 5 percent concentration is 0.5 percent. For concentrations in the 1 to 1000 ppmvC range, a FID was used. The precision at 9.5 ppmv is 1.0 percent. EAS maintains a complete line of commercial light hydrocarbon standards spanning the range of 10 ppmv to 10 percent. The results were integrated using an HP 3393A integrator and the concentrations of the individual hydrocarbons were determined by transferring the integrated areas into a HP 150 computer using a LOTUS 1-2-3 spreadsheet.

5.1.3 Heavy hydrocarbon and Oxygenates Analysis (C5 to C10)

The heavy hydrocarbons and oxygenates (aldehydes and ketones) were analyzed using an HP 5890 with a fused silica capillary column. This method was described in Sing (1980). This publication describes the use of a canister-based system in conjunction with a freezeout loop for the analysis of sub-par billion hydrocarbons and stable oxygenates. The analysis procedure is similar to that used by Westburg (1984) and Rasmussen (1987). The capillary column provides the required resolution to separately identify the individual reactive organic compounds. Major components that cannot be identified using FID were analyzed for confirmation on an HP 5890/5970 GC/MSD system as described in EPA Method TO-14. A diagram for the instrumental set-up is shown in Figure 5.1.2. The heavy hydrocarbons are analyzed by passing the sample through a Nafion dryer into the 8" glass bead freezeout loop immersed in liquid oxygen. The components are desorbed into a fused silica cryofocussing loop with 80 °C hot water. They are then desorbed from the cryofocus loop and the components are separated using a 100-meter 0.25micron fused silica capillary column with a 0.5-micron coating. The column is programmed from -20 °C to 200 °C at 3 °C/min. Total analysis time is 60 minutes The method detection limit for this method is about 0.1 ppbvC for most compounds and the analytical precision at 10 ppbvC is 5 percent. The compounds are detected on a FID set to operate at high sensitivity A detailed description of the analytical procedure is given in section 5.2.3. Chromatograms were integrated using an HP 3393A computing integrator and stored on a HP 9114 disk drive for reintegration or further examination if required at a later date. Compounds were calibrated using an NBS-traceable propane/hexane/benzene standard. On the FID, hydrocarbons have a uniform response based on the number of carbon atoms. Data from the integrator were entered into a LOTUS 1-2-3 spreadsheet to generate the final report.



5.1.4 Compound Analysis and Identification

The GC/MS method (EPA Method TO-14) uses a cryotrapping system and a high resolution capillary column to analyze for volatile organic compounds.

A diagram of the analytical system, with an HP 5970 MSD for the detector, is shown in Figure 5.1.3. A 100 to 1000 mL gaseous sample is introduced from the air sampling canister through a Nafion dryer to the freezeout loop. The freezeout loop is immersed in liquid oxygen and concentrates the air sample. After the sample is loaded, it is cryofocussed onto the beginning of a 30 meter fused silica capillary column. The cryofocused loop is then warmed and the compounds are separated and enter the mass spectrometer. The GC/MS has a complete data system capable of collecting, storing, and interpreting the data collected. The GC/MS is tuned and operated according to the specifications outlined in EPA SW 846 Test Methods. Compounds were calibrated by the external standard procedure using a NBS traceable Scott-Marrin air standards. The relative standard deviation of the method is 20% at 5 ppbv and the MDL is 0.5 ppbv for most compounds.

5.1.5 Permanent Gases (Nitrogen, Oxygen, Carbon Dioxide, Methane)

The permanent gases were analyzed by a SCAQMD method using a GC with a thermal conductivity detector and a FID on a Molecular Sieve 5A column a Poropak Q/N column mix. the system uses a 1 mL sample loop and is set-up with column backflush and bypassing to simultaneously measure the Carbon Dioxide and other fixed gases. The instrument is run isothermally at 70°C with helium carrier gas and has a detection limit of 0.05%. For low levels of Carbon Dioxide a catalyst is used to convert the Carbon Dioxide to Methane for analysis.

5.1.6 Aldehydes by the DNPH method

The C1 to C4 aldehydes were analyzed by a modification of EPA Method TO5. This method is based on the reaction of low molecular weight aldehydes and ketones with 2,4-dinitrophenylhydrazine to form stable derivatives. The source gases were sampled using midget impingers filled with acidified DNPH in acetonitrile. An aliquot of the impinger contents was analyzed using high performance liquid chromatography. The analytical column used was a Supelcosil LC18 reverse phase type, with a Supelco guard column. The system was run isocratically, using 70% methanol / 30% water as the eluant. The sample, typically 15 microliters, was injected with a Pressure-Lok syringe. The aldehydes were detected using a UV-visible detector operating at a wavelength of 360 nm, and quantified using an HP 3393A computing integrator.

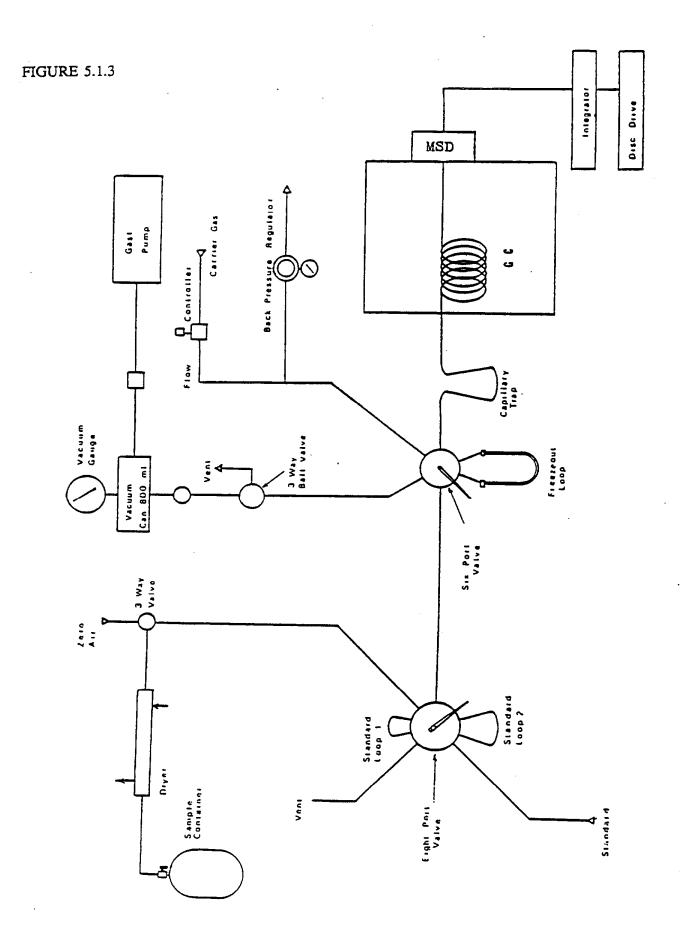
5.2 Analytical Standard Operating Procedures

5.2.1 Methane Analysis

1. Standards

This procedure is used to load standards at high concentrations (5 ppmv) and have them diluted using calibrated loops to give GC responses equivalent to ambient concentrations. Dilution is 1/1000 with an uncertainty of less than 5%.

- a. Set system to operating parameters given in Table 5.1.b.
- b. Light FID, and place sample valve in load position.



- c. Connect standard cylinder to sampling line.
- d. Open valve on standard cylinder and let bubble for 3 seconds to flush loop. Close valve.
- e. Rotate sample valve to inject position, start integrator.
- f. At end of run turn sample valve to load position.
- g. Disconnect standard cylinder.

2. Ambient Air Samples

This procedure can be used to load low pressure samples in stainless steel sample canisters, and to load low pressure standards at simulated ambient concentrations.

- a. Set system to operating parameters given in Table 5.1.b.
- b. Light FID, turn sample valve to load position.
- c. Connect sample canister to sampling line.
- d. Open valve on sample canister, and let bubble for 3 seconds to flush loop. Close valve.
- e. Turn sample valve to inject, and start integrator.
- f. At the end of the run, turn sample valve to load.
- g. Disconnect sample canister from sample intake line, record can pressure, place cap on sample canister, and place on table for light hydrocarbon analysis.

5.2.2 Light Hydrocarbon Analysis

This procedure is used to load standards at high concentrations (5 ppmv) and have them diluted using calibrated loops to give GC responses equivalent to ambient concentrations. Dilution is 1/1000 with an uncertainty of less than 5%.

- a. Set system to operating parameters given in Table 6.1.b.
- b. Light FID, turn on vacuum pump, turn on hot water, pour one Dewar of liquid oxygen, and place sample valve in the load position.
- c. Open vacuum valve and evacuate volume measuring canister to 22.0".
- d. Turn air sampling valve to zero air position.
- e. Connect standard input line of 6 port standard valve to standard cylinder. Set regulator on standard cylinder to 10 psig. Open regulator valve.
- f. Flush sample loop with zero air by opening intake valve and turning selector to vacuum. After a drop of 2" vacuum turn standard valve to load position. Turn selector to off and close intake valve. Re-evacuate volume measuring canister to 22".

- g. Place freezeout loop in liquid oxygen Dewar.
- h. Open valve on standard cylinder and let bubble for 3 seconds to flush loop. Close valve.
- i. Rotate standard valve to inject position, turn selector to vacuum.
- j. Let pressure rise until it reaches 10". This corresponds to a zero air volume of 500 mL.
- k. Close intake valve first then turn selector to off. Close valve on sample can.
- I. Turn sample valve to inject, remove liquid oxygen and immediately place freezeout loop in hot water bath and start integrator.
- m. At end of run, turn sample valve to load position and remove hot water bath.
- n. Turn regulator on standard cylinder off, and close regulator valve. Disconnect standard cylinder.

2. Ambient Air Samples

This procedure can be used to load low pressure samples in stainless steel sample canisters, and to load low pressure standards at simulated ambient concentrations.

- a. Set system to operating parameters given in Table 5.1.b.
- b. Light FID, turn on vacuum pump, turn on hot water, pour a Dewar of liquid oxygen, and place sample valve in the load position. Turn sampling line open to sample position.
- c. Open vacuum valve and evacuate volume measuring canister to 22.0".
- d. Connect sample canister to intake line.
- e. Open intake valve and turn selector to vacuum and flush system and glass bead freezeout loop to 22" vacuum.
- f. Close intake valve, and turn selector to off. Re-evacuate volume measuring canister to 22.0". Flush system with small amount of sample by opening selector valve and sample canister and re-evacuate volume measuring canister to 22.0".
- g. Place freezeout loop in liquid oxygen Dewar.
- h. Open valve on sample canister.
- i. Turn selector to vacuum and open intake valve. Let pressure rise in volume measuring canister until it reaches 10". This corresponds to a sample size of 500 mL.
- j. Close intake valve first then turn selector to off. Close valve on sample canister.
- k. Turn sample valve to inject, remove liquid oxygen Dewar replace with hot water bath, and start integrator.

- l. At end of run turn sample valve to inject position, and remove hot water bath.
- m. Disconnect sample canister from sample intake line, record can pressure, place cap on sample canister, and place on table for heavy hydrocarbon analysis.

5.2.3 Heavy Hydrocarbon Analysis

1. Hydrocarbon Standards

This procedure is used to load standards at high concentrations (5 ppmv) and have them diluted using calibrated loops to give GC responses equivalent to ambient concentrations. Dilution is 1/1000 with an uncertainty of less than 5%.

- a. Set system to operating parameters given in Table 5.1.b.
- b. Light FID, turn on vacuum pump, turn on hot water, pour two Dewars of liquid oxygen, and place sample valve in the load position.
- c. Open vacuum valve and evacuate volume measuring canister to 24.5".
- d. Turn intake valve to "zero air" position.
- e. Connect standard input line of 8 port standard valve to standard cylinder. Set regulator on standard cylinder to 10 psig. Open regulator valve.
- f. Flush both sample loops with zero air by opening intake valve and turning selector to vacuum. After a drop of 2" vacuum turn standard valve to flush other loop. After an additional 2" vacuum drop turn selector to off and close intake valve. Leave standard valve in position for desired loop size. Re-evacuate volume measuring canister to 24.5".
- g. Open valve on standard cylinder and let bubble for 3 seconds to flush loop. Close valve.
- h. Place freezeout loop in liquid oxygen Dewar.
- i. Rotate standard valve and turn selector to vacuum.
- j. Let pressure rise until it reaches 14". This corresponds to a zero air volume of 500 mL.
- k. Turn selector to off. Close valve on standard cylinder.
- I. Place capillary loop in liquid oxygen Dewar.
- m. Set timer for 2.5 min, and turn sample valve to inject.
- n. Remove liquid oxygen and place freezeout loop in hot water bath. Start timer.
- o. At 1.5 min set initial oven temperature to -20° C.
- p. After 2.5 min and oven temperature of -20° C, turn sample valve to load position, start integrator, and simultaneously pull out capillary loop.
- q. Remove hot water from freezeout loop.

- r. Turn cryo valve off at 25° C. CLEAR. ENTER OFF.
- s. Disconnect standard cylinder. Turn regulator on standard cylinder off, and close regulator valve.

2. Ambient Air Standards

This procedure can be used to load low pressure samples in stainless steel sample canisters, and to load low pressure standards at simulated ambient concentrations.

- a. Set system to operating parameters given in Table 5.1.b.
- b. Light FID, turn on vacuum pump, turn on hot water, pour two Dewars of liquid oxygen, and place sample valve in the load position.
- c. Open vacuum valve and evacuate volume measuring canister to 24.0".
- d. Turn intake valve to "sample" position.
- e. Open intake valve and turn selector to vacuum and flush system and glass bead freezeout loop to 22" vacuum.
- f. Close intake valve, and turn selector off. Re-evacuate volume measuring canister to 24.5".
- g. Flush system with a small amount of sample by turning selector to vacuum, open sample canister and let pressure rise to 22". Close sample canister, and turn selector to off. Re-evacuate volume measuring canister to 24.5".
- h. Place freezeout loop in liquid oxygen Dewar.
- i. Open valve on sample canister.
- j. Turn selector to vacuum and let pressure rise in volume measuring canister until it reaches 14". This corresponds to a sample size of 500 mL.
- k. Turn selector to off. Close valve on sample canister.
- l. Place capillary loop in liquid oxygen Dewar.
- m. Set timer for 2.5 min, and turn sample valve to inject.
- n. Remove liquid oxygen, place freezeout loop in hot water bath and simultaneously start timer.
- o. At 1.5 min set initial oven temperature to -20° C.
- p. After 2.5 min and oven temperature of -20° C, turn sample valve to load position, start integrator, and simultaneously pull our freezeout loop.
- q. Remove hot water from freezeout loop.
- r. Turn cryo valve off at 25° C. CLEAR. ENTER OFF.

s. Disconnect sample canister from sample intake line, record can pressure, place cap on sample canister, and place on temporary storage shelf.

5.2.4 Attachment 1 Compounds by GC/MS

1. Standards

This procedure is used to load standards at high concentrations (5 ppmv) and have them diluted using calibrated loops to give GC responses equivalent to ambient concentrations. Dilution is 1/500 with an uncertainty of less then 5%.

- a. Set system to operating parameters.
- b. Turn on vacuum pump, turn on hot water, and pour two Dewars of liquid oxygen, and place Sample Valve in the load position.
- c. Open Vacuum Valve and evacuate Volume Measuring Canister to 24.5".
- d. Turn Intake Valve to "aero air" position.
- e. Connect Standard Input Line of 8 port Standard Valve to standard cylinder. Set regulator on standard cylinder to 10 psig. Open regulator valve.
- f. Flush both sample loops with zero air by opening Intake Valve and turning Selector to vacuum. After a drop of 2" vacuum turn standard valve to flush other loop. After an additional 2" vacuum drop turn Selector to off and close Intake Valve. Leave Standard Valve in position for desired loop size. Re-evacuate Volume Measuring Canister to 24.5".
- g. Open valve on standard cylinder and let bubble for 3 seconds to flush loop. Close valve.
- h. Place freezeout loop in liquid oxygen Dewar.
- Rotate Standard Valve and turn Selector to vacuum.
- j. Let pressure rise until it reaches 14". This corresponds to a zero air volume of 500 mL.
- k. Turn Selector to off. Close valve on standard cylinder.
- l. Place capillary loop in liquid oxygen Dewar.
- m. Set timer for 2.5 min, and turn Sample Valve to inject.
- n. Remove Liquid Oxygen and place freezeout loop in hot water bath. Start timer.
- o. On GC/MS computer enter the data acquisition program and set up data collection file for standard. Standard files are formatted as: S (Days Date) (Last digit of year) A (Run Number). D Turn on cryo option, and enter the Prepare To Inject Program.
- p. After 2.5 min and oven temperature of -20° C, turn Sample Valve to load position, hit the GO softkey on the computer, and simultaneously pull out capillary loop.

- q. Remove hot water from Freezeout loop.
- r. Turn cryo valve off at 25° C. CLEAR. ENTER OFF.
- s. Disconnect standard cylinder. Turn regulator on standard cylinder off, and close regulator valve.

2. Ambient Air Standards

This procedure can be used to load low pressure samples in stainless steel sample containers, and to load low pressure standards at simulated ambient concentrations.

- a. Set system to operating parameters given in Table 1.
- b. Open Vacuum Valve and evacuate Volume Measuring Canister to 24.0".
- c. Turn Intake Valve to "sample" position.
- d. Open Intake Valve and turn Selector to vacuum and flush system and glass bead Freezeout Loop at 22" vacuum.
- e. Close Intake Valve, and turn selector to off. Re-evacuate Volume Measuring Canister to 24.5".
- f. Flush system with a small amount of sample by turning Selector to vacuum, open Sample Canister and let pressure rise to 22". Close Sample Canister, and turn Selector to off. Re-evacuate Volume Measuring Canister to 24.5".
- g. Place Freezeout Loop in liquid oxygen Dewar.
- h. Open valve on Sample Canister.
- i. Turn Selector to vacuum and let pressure rise in Volume Measuring Canister until it reaches 14". This corresponds to a sample size of 500 mL.
- j. Turn Selector to off. Close valve on Sample Canister.
- k. Place Capillary Loop in liquid oxygen Dewar.
- 1. Set timer for 2.5 min, and turn Sample Valve to inject.
- m. Remove liquid oxygen, place Freezeout Loop in hot water bath and simultaneously start timer.
- n. On GC/MS computer enter the data acquisition program and set up data collect ion file for standard. Standard files are formatted as: S(Days Date)(Last digit of year)A(Run Number).D Turn on cryo option, and enter the Prepare To Inject Program.
- o. After 2.5 min and oven temperature of -20°C, turn Sample Valve to load position, hit the GO softkey on the computer, and simultaneously pull out capillary loop. Min set initial oven temperature to-20°C.
- p. Remove hot water from Freezeout Loop.

- q. Turn cryo valve off at 25° C. CLEAR. ENTER OFF.
- r. Disconnect Sample Canister from Sample Intake Line, record can pressure, place cap on Sample Canister, and place on temporary storage shelf.

5.2.5 Permanent Gases

Standards

- a. Set system to operating parameters.
- b. Light FID, turn on TCD, and place sample valve in load position.
- c. Connect standard cylinder to sampling line.
- d. Open valve on standard cylinder and let bubble for 3 seconds to flush loop. Close valve.
- e. Rotate sample valve to inject position, start integrator.
- f. Turn second column valve to out position at 1.6 min.
- g. Turn second column valve to in position at 8.0 min.
- h. At end of run turn sample valve to load position.
- Disconnect standard cylinder.

2. Ambient Air Samples

This procedure can be used to load low pressure samples in stainless steel sample canisters, and to load low pressure standards at simulated ambient concentrations.

- a. Set system to operating parameters.
- b. Light FID, turn on TCD, and turn sample valve to load position.
- c. Connect sample canister to sampling line.
- d. Open valve on sample canister, and let bubble for 3 seconds to flush loop. Close valve.
- e. Turn sample valve to inject, and start integrator.
- f. Turn second column valve to out position at 1.6 min.
- g. Turn second column valve to in position at 8.0 min.
- h. At the end of the run, turn sample valve to load.
- i. Disconnect sample canister from sample intake line, record can pressure, place cap on sample canister, and place on table for light hydrocarbon analysis.

5.3 Calibration Standards

There are two types of calibrations performed for the hydrocarbon analysis. One is for the amount of the various hydrocarbons present and the second is for the identification of the retention times of the different hydrocarbons species.

5.3.1 Quantitative Standards

The concentrations of the individual hydrocarbons were determined by their uniform carbon response on the FID. This procedure is the recommended calibration Dprocedure and has been shown to be accurate to 5 to 8% (Lonneman, 1979). The primary calibration standard used for the light and heavy hydrocarbons is a NBS traceable reference gas standard obtained from Scott-Marrin, Riverside, CA. The specifications of the standard are shown in Figure 5.3.1.(a) the light hydrocarbon fraction is calibrated against propane and the non-aromatic fraction of the heavy hydrocarbons are calibrated against hexane. The aromatic hydrocarbons are calibrated against benzene. The standard cylinder is returned every year for recalibration by the manufacturer. The concentrations of the hydrocarbons in the standard are converted to parts per billion carbon (ppbC) using the procedure described by Westbert et. al. (1984).

The concentrations of the individual compounds are determined by using an External Calibration procedure, in which the compound's response is compared to the response of a standard. The primary calibration standard is an NIST traceable reference gas standard obtained from Scott-Marrin, Inc., Riverside, CA. The specifications of the standard are shown in Figure B.5.3.1(b) & (c) The standard cylinder is returned every six months for recalibration by the manufacturer. In addition, a standard containing toluene, o-xylene, ethene and propene is used to verify response for these compounds.

Standards for aldehyde determinations were prepared as described in ARB Method 110.

Intercomparison of the light and heavy hydrocarbon runs can be made using both the propane peak and the hexane peak. The propane peak can be used because the heavy loaded column is capable of separating the lighter hydrocarbons.

5.3.2 Qualitative Calibration

The retention times were calibrated against commercial gas standard blends of different hydrocarbons and from laboratory standards prepared from neat materials.

The commercial gas blends are available from Ideal Gas Products and Scott Specialty Gases. These standards are used to establish retention times and to check concentrations obtained from the NBS traceable standard.

Laboratory standards are prepared from pure materials for those compounds not available in gas blends. Known quantities of the pure materials are diluted with a measured volume of "zero air". Dilutions are made in stainless steel canisters and are stable for use in retention time calibrations for several months.



REPORT OF ANALYSIS

то:	Steve Hoyt Environmental Analytical Scients 3576 Empleo St., Suite 5 San Luis Obispo, CA 93401	DATE: 23 October 1986
	R ORDER NUMBER: 1171	manamana kanamana ka
CYLINDER COMPONE Propane n-Hexane Benzene Nitroger	CC121 CONCENTRATION(v/v) 4.71 ± 0.05 ppm 5.12 ± 0.1 ppm 5.01 ± 0.1 ppm	CYLINDER NUMBERCOMPONENT CONCENTRATION(v/v)
CYLINDE	R NUMBER	CYLINDER NUMBER COMPONENT CONCENTRATION(v/v
ANALYS	т <u>//// (/ // // // // // // // // // // //</u>	APPROVED

company without extra cost.



REPORT OF ANALYSIS

TO:

DATE:

Steve Hoyt

Environmental Analytical Services

3576 Empleo, Suite #5

San Luis Obispo, CA 93401

5 November 1987

CUSTOMER ORDER NUMBER: 1253

CYLINDER NUMBER	CC62416
COMPONENT	CONCENTRATION(v/v)
inyl Chloride	$5.14 \pm 0.1 \text{ ppm}$
l loromethane	5.25 ± 0.1 ppm
richloromethane	$0.515 \pm 0.01 \text{ ppm}$
Dichloroethane	5.20 ± 0.1 ppm
1-Trichloroethane	$0.520 \pm 0.01 \text{ ppm}$
etrachloromethane	0.525 ± 0.01 ppm
hloroethylene	$0.530 \pm 0.01 \text{ ppm}$
enzene	5.25 ± 0.1 ppm
Dibromoethane	5.29 ± 0.1 ppm
· achloroethylene	$0.530 \pm 0.01 \text{ ppm}$
.trogen	Balance

M. Dodd

The only liability of this company for gas which fails to cor company without extra cost.

APPROVED

J. T. Marrin

talysis shalf be replacement or reenalysis thereof by the



REPORT OF ANALYSIS

TO:

DATE:

12 September 1988

Steve Hoyt Environmental Analytical Services 3576 Empleo Street, Ste. 5 San Luis Obispo, CA 93401

CUSTOMER ORDER NUMBER: 1367

CYLINDER NUMBER

CC68692

COMPONENT

CONCENTRATION(v/v)

Halocarbon-12

5.20 ±20.1 ppm

Halocarbon-11

 $4.40 \pm 0.1 \text{ ppm}$

1,1-Dichloroethylene 4.37 ± 0.1 ppm

1,1-Dichloroethane

 $5.05 \pm 0.1 \text{ ppm}$

1,1,2-Trichloroethane 5.20 ± 0.1 ppm

Nitrogen

Balance

The only liability of this company for gas which fails to cocompany without extra cost.

analysis shall be replacement or reanalysis thereof by the

5.4 Calibration Procedures

5.4.1 Methane

The methane analyzer was calibrated by passing the methane standard through a 1.0 mL calibrated sample loop. The standard was then injected onto the column according to the standard operating procedures. The concentration of the methane is determined using the following formula.

Methane (ppmC) = Standard Conc. (ppmv) * 1 * (Sample Area/Standard Area)

The factor of one accounts for the one carbon atom in methane.

5.4.2 Hydrocarbons

The light and heavy hydrocarbons were calibrated by using a dilution of the 5 ppm NBS traceable standard. A summary of the calibration procedures is shown in Table 5.4.2. The daily calibration consists of a zero point and two calibration points (10% and 100% of range). One calibration point is run at the beginning of the dat and one at the end of the day. Weekly, a three point calibration is run to verify the linearity of the instrument. During the monthly internal audit of the analytical system a 5 point calibration curve is run to establish performance criteria for the system.

Standards were prepared using a gas dilution system on the gas chromatograph or by making static dilutions to atmospheric levels. The gas dilution system is constructed from an 8 port gas sampling valve with a 0.05 mL, 0.5 mL, and 5.0 sample loops. The loops are filled with the standard and flushed with "zero air" prepared with an AADCO Model 737 pure air generator. The three loop sizes are used to prepare a three point calibration of the system to check the linearity in the concentration range of interest. The gas dilution system is used for the daily instrument calibration. The concentration of the individual hydrocarbons is determined using the following formula:

Hydrocarbon (ppbC) = Standard Conc. (ppbv) * number of carbons * (Sample Area/Standard Area)

Standards at atmospheric concentration levels were prepared by diluting the NBS traceable standard in stainless steel canisters. The standards are diluted by using a calibrated syringe to inject a measured volume of NBS traceable standard into a passivated stainless steel canister. The canister is filled with a known volume of zero air measured using a mass flow meter. The diluted standards are run in exactly the same manner as the samples and serve as a check of the sample concentration and injection system.

5.4.3 GC/MS Compounds

The GC/MS Compounds were calibrated using a dilution of the NBS traceable standard. The daily calibration consists of a zero point and two calibration points (10% and 100% of range). One calibration point is run at the beginning of the day and one at the end of the day. Weekly, a three point calibration is run to verify the linearity of the instrument. During the monthly internal audit of the analytical system a 5 point calibration curve is run to establish performance criteria for the system.

Standards were by using a gas dilution system on the gas chromatograph or by making static dilutions to atmospheric levels. The gas dilution system is constructed from an 8 port gas sampling valve with a 0.05 mL, 0.5 mL, and 5.0 sample loops. The loops are filled with the standard and flushed with "zero air" prepared with an AADCO Model 737 pure air generator. The three loop sizes are used to prepare a three point calibration of the system to check the linearity in the concentration range of interest. The gas dilution system is used for the daily instrument calibration.

The concentration of the individual hydrocarbons is determined using the following formula:

Compound (ppbv) = Std. Conc. (ppbv) * (Sample Area/Std. Area) * (Std. Volume/Sample Volume)

Standards at atmospheric concentration levels were prepared by diluting the NBS traceable standard in stainless steel canisters. The standards were diluted using a calibrated syringe to inject a measured volume of the NBS traceable standard into a passivated stainless steel canister. The canister is filled with a known volume of zero air measured using a mass flow meter. This ambient level standard is sent to another laboratory for calibration against the NBS 5 ppbv VOC standard. The diluted standard is run in exactly the same manner as the samples and serves as a check of the sample concentration injection system.

REPORT DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188 Design reporting durgen for this collection of information is estimated to average. I hour per response, including the time for reviewing instructions, searching existing data source and the property of the control o activities and find that is the sata needed. and completing and relevange the collection of information. Send comments reparation to source estimate or any other aspect of the ending of information including suggestions for regulging this purgent. Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jeffers, by Service 224 His outcome Levice 222-302, and to the just the or Management and sudder Mapermork Reduction Projects (CAL) (183). Washington, DC 20503. 1. «GENCY USE CINLY Leave Drank) | 2. REPORT DATE 3. REPORT TYPE AND DATES COVERED PB92-170026 April 30, 1991 Final Report A TITLE AND SUBTITLE 5. FUNDING NUMBERS Development of Species Profiles for Selected Organic Emissions Sources A832-059 Volumes I and 5. AUTHOR(S) 7. PERFORMING CRGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER California Polytechnic State University Chemistry Department 9. SPONSORING, MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSORING / MONITORING California Air Resources Board AGENCY REPORT NUMBER Research Division 1800 15th Street Sacramento, CA 95814 ARB/R-92/ 483 11. SUPPLEMENTARY NOTES 12a. DISTRIBUTION / AVAILABILITY STATEMENT 12b. DISTRIBUTION CODE Release unlimited. Available from National Technical Information Service 5285 Port Royal Road, Springfield, VA 22161 13. ABSTRACT (Maximum 200 words) Hydrocarbon species profiles were developed for selected petroleum production equipment emissions and for exhaust from utility and heavy-duty engines. Emissions from petroleum production facilities were collected from wellheads, pipelines, and processing and storage systems. Engine exhaust emissions were collected using a portable dilution tunnel system. Analyses of C1 through C10 hydrocarbons were performed using gas chromatographic methods and aldehydes were analyzed by the dinitrophenyl hydrazine method. 14. SUBJECT TERMS
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